

John E. McMurry • Robert C. Fay

General Chemistry: Atoms First

Chapter 5 Covalent Bonds and Molecular Structure

Lecture Notes

Alan D. Earhart

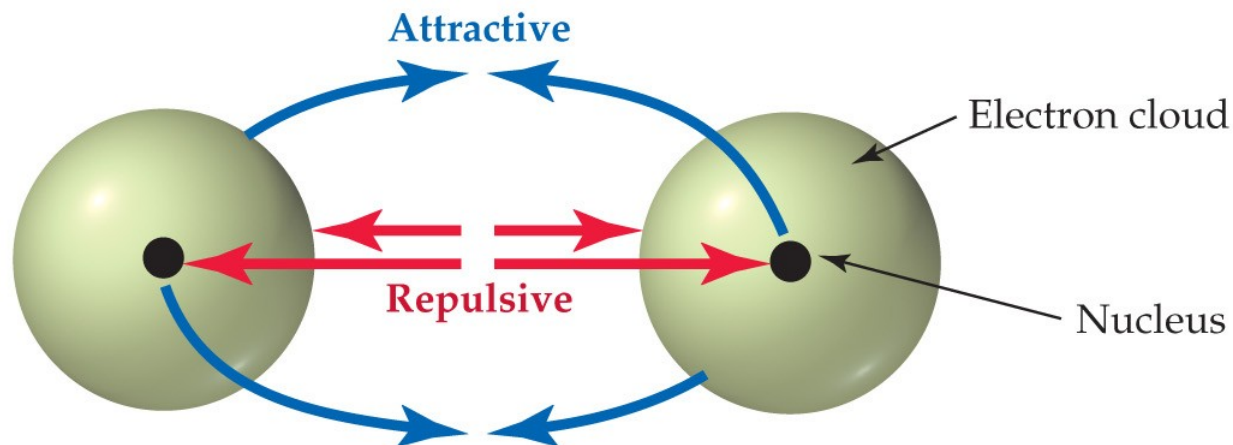
Southeast Community College • Lincoln, NE

Molecules and the Covalent Bond

Covalent Bond: A bond that results from the sharing of electrons between atoms.

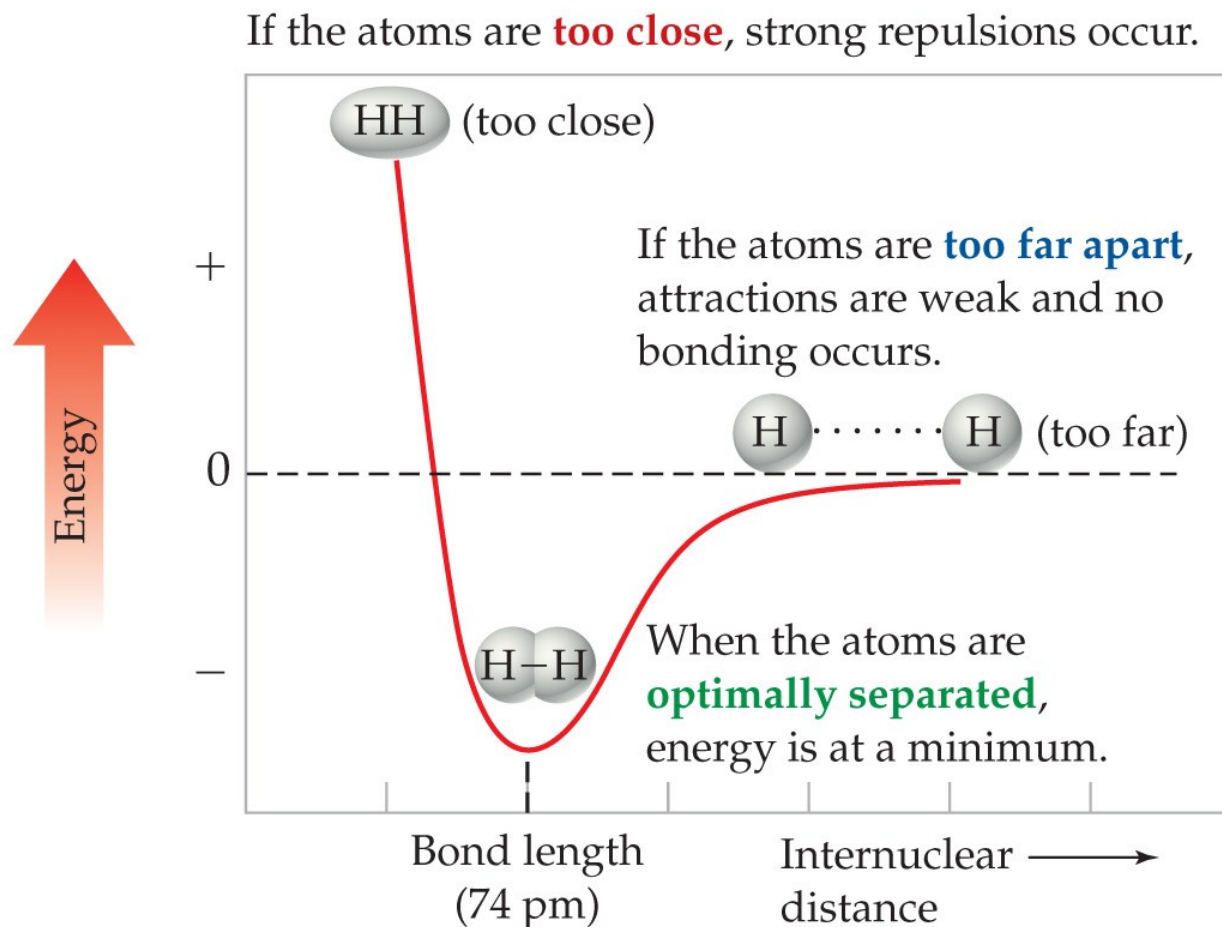
Molecule: The unit of matter (atoms) held together by covalent bonds.

Molecules and the Covalent Bond



The nucleus–electron **attractions** are greater than the nucleus–nucleus and electron–electron **repulsions**, resulting in a net attractive force that binds the atoms together.

Molecules and the Covalent Bond



Strengths of Covalent Bonds

TABLE 5.1 Average Bond Dissociation Energies, D (kJ/mol)

H—H	436 ^a	C—H	410	N—H	390	O—H	460	F—F	159 ^a
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243 ^a
H—F	570 ^a	C—F	450	N—F	270	O—F	180	Br—Br	193 ^a
H—Cl	432 ^a	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151 ^a
H—Br	366 ^a	C—Br	270	N—Br	240	O—Br	210	S—F	310
H—I	298 ^a	C—I	240	N—I	—	O—I	220	S—Cl	250
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225
H—S	340	C—S	260	N—S	—	O—S	—		
Multiple covalent bonds ^b									
C=C	728	C≡C	965	C=O	732	O=O	498 ^a	N≡N	945 ^a

^aExact value.

^bWe'll discuss multiple covalent bonds in Section 5.6.

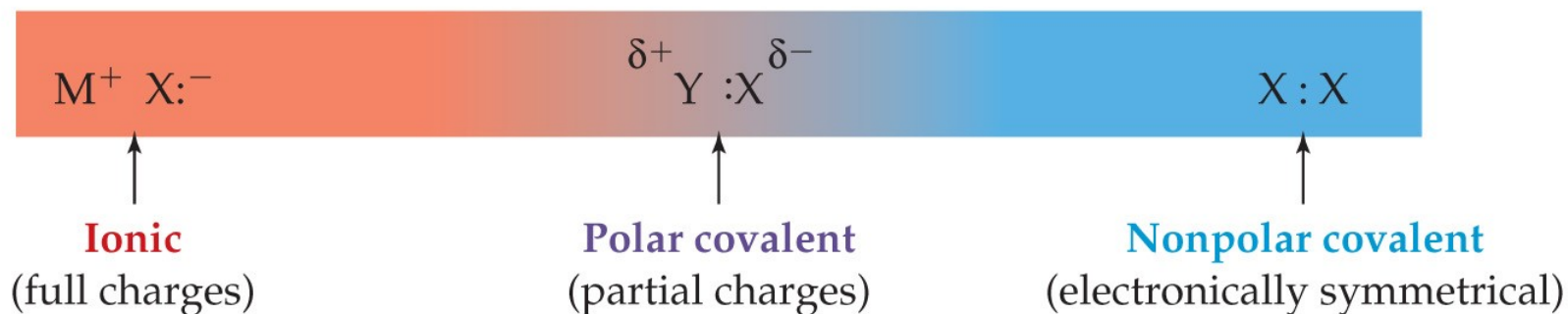
A Comparison of Ionic and Covalent Bonds

TABLE 5.2 Some Physical Properties of NaCl and HCl

Property	NaCl	HCl
Formula mass	58.44 amu	36.46 amu
Physical appearance	White solid	Colorless gas
Type of bond	Ionic	Covalent
Melting point	801 °C	−115 °C
Boiling point	1465 °C	−84.9 °C

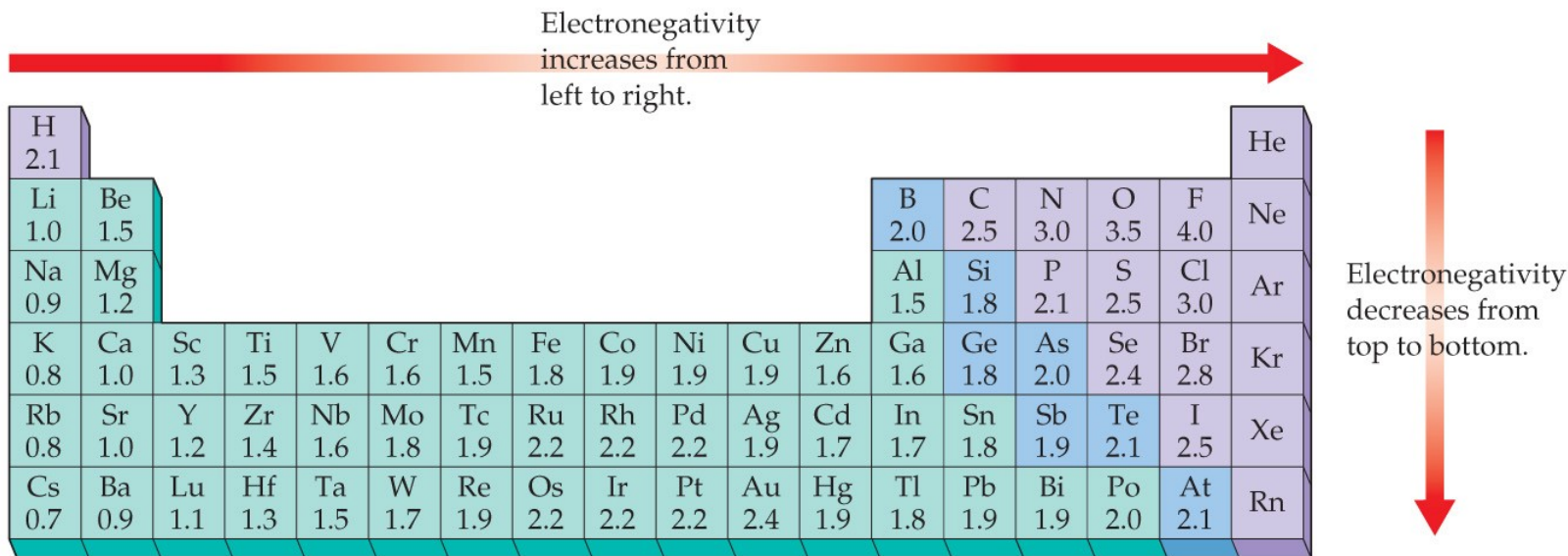
Polar Covalent Bonds: Electronegativity

Electronegativity: The ability of an atom in a molecule to attract the shared electrons in a



Polar covalent bonds have an unsymmetrical electron distribution in which the bonding electrons are attracted more strongly by one atom than the other.

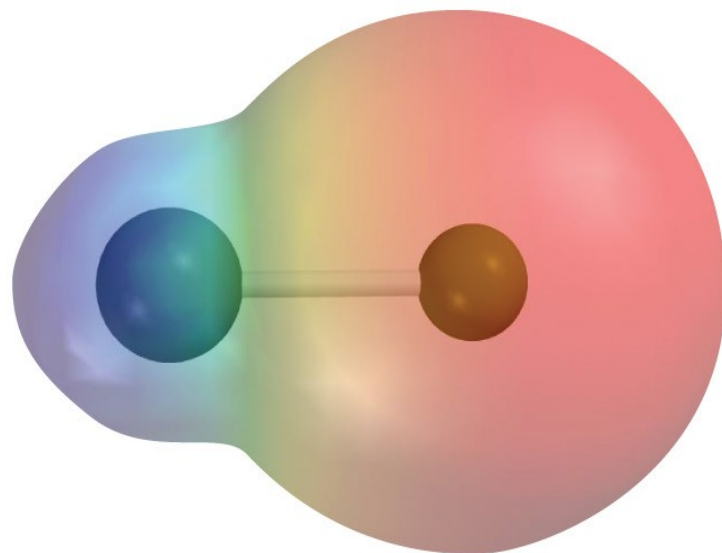
Polar Covalent Bonds: Electronegativity



Polar Covalent Bonds: Electronegativity



An ionic bond

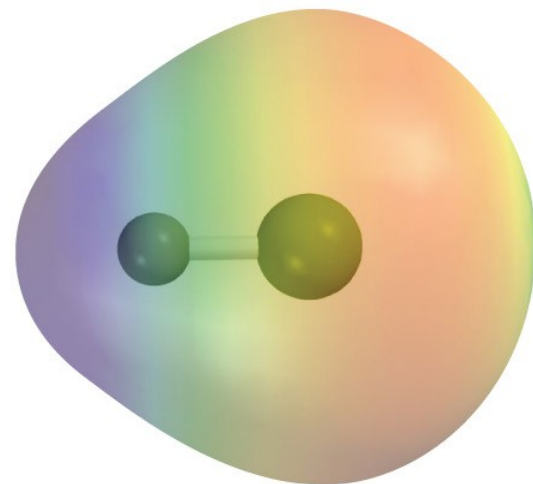


Polar Covalent Bonds: Electronegativity



↖ A polar covalent bond.

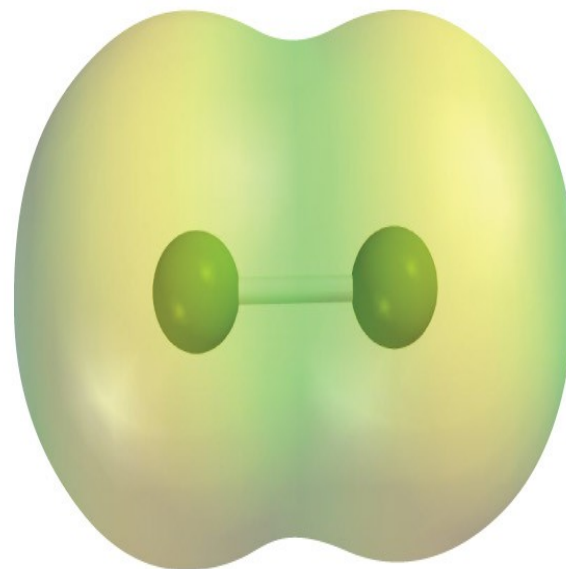
The bonding electrons are attracted more strongly by Cl than by H.



Polar Covalent Bonds: Electronegativity



A nonpolar covalent bond



Naming Molecular Compounds

TABLE 5.3 Numerical Prefixes for Naming Compounds

Prefix	Meaning
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

Because nonmetals often combine with one another in different proportions to form different compounds, numerical prefixes are usually included in the names of binary molecular compounds.

Naming Molecular Compounds



The first element listed is more cationlike and takes the name of the element.

The second element listed is more anionlike and takes the name of the element with an “ide” modification to the ending.

The prefix is added to the front of each to indicate the number of each atom.

dinitrogen tetraoxide

Electron-Dot Structures

Electron-Dot Structures (Lewis Structures):

A representation of an atom's valence electrons by using dots and indicates by the placement of dots how the valence electrons are distributed in the molecule.

Electron-Dot Structures



Two hydrogen
atoms

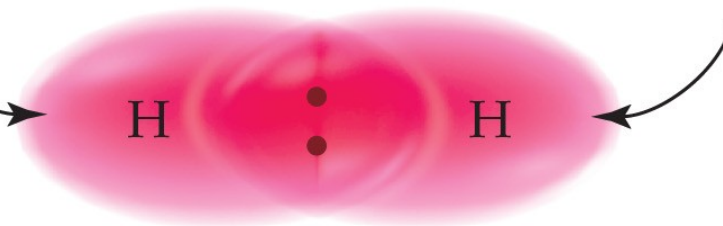


A hydrogen
molecule

An electron-pair bond

This hydrogen shares
an electron pair ...

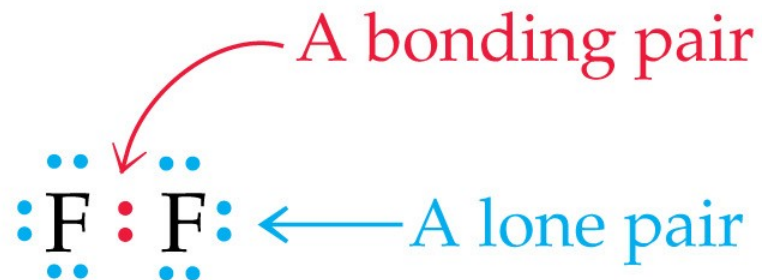
... and this hydrogen
shares an electron pair.



Electron-Dot Structures

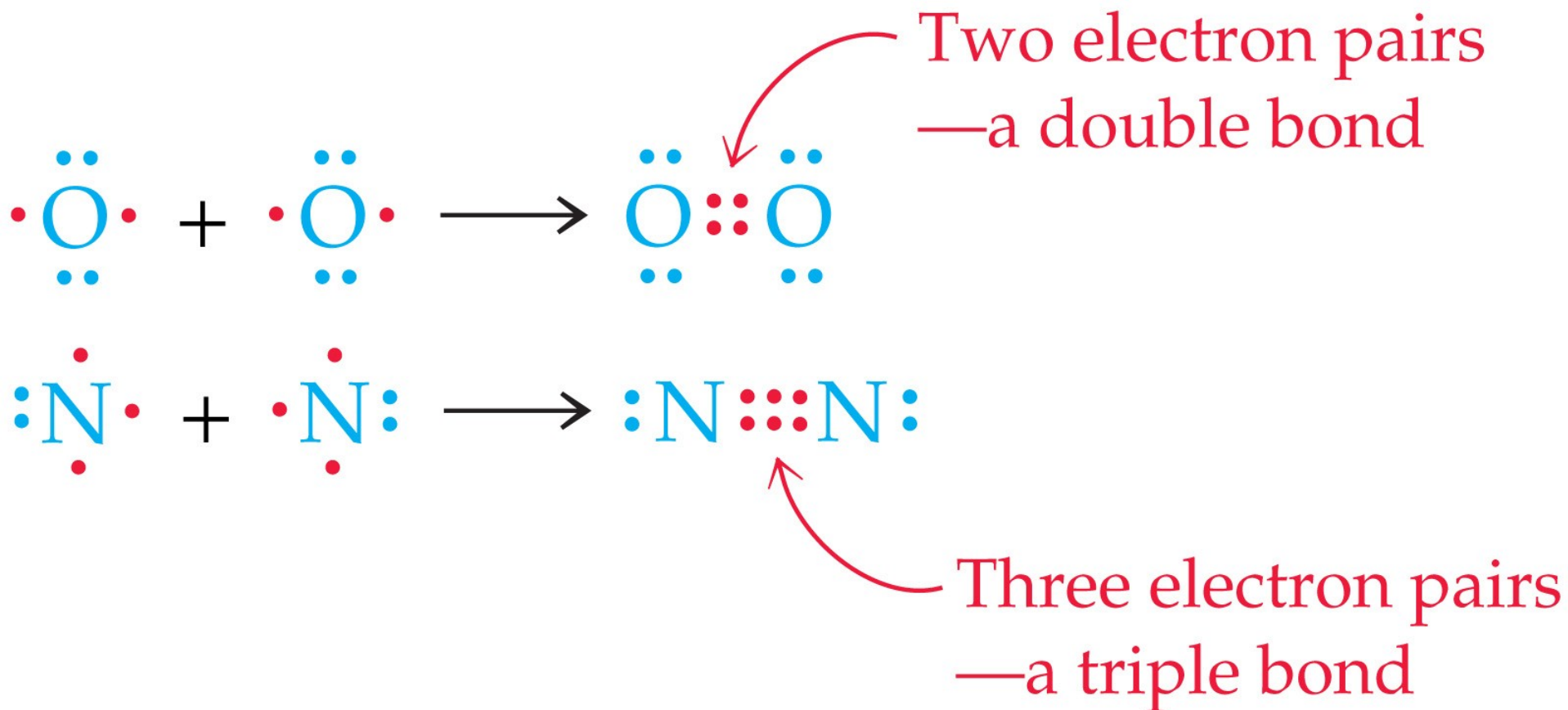


Two F atoms
(seven valence electrons
per atom)



An F₂ molecule
(each F is surrounded
by eight valence electrons)

Electron-Dot Structures



Electron-Dot Structures of Polyatomic Molecules

Step 1: Valence Electrons

- Count the total number of valence electrons for all atoms in the molecule.
- Add one additional electron for each negative charge in an anion or subtract one for each positive charge in a cation.

TABLE 5.4 Covalent Bonding for Second-Row Elements

Group	Number of Valence Electrons	Number of Bonds	Example
3A	3	3	BH ₃
4A	4	4	CH ₄
5A	5	3	NH ₃
6A	6	2	H ₂ O
7A	7	1	HF
8A	8	0	Ne

Electron-Dot Structures of Polyatomic Molecules

Step 2: Connect Atoms

- Draw lines to represent bonds between atoms.
- For hydrogen and second row atoms, use the number of bonds listed below.
- For third row and greater atoms, they may have more bonds than predicted by the octet rule.
- The least electronegative atom is usually the central atom.

TABLE 5.4

Covalent Bonding for Second-Row Elements

Group	Number of Valence Electrons	Number of Bonds	Example
3A	3	3	BH ₃
4A	4	4	CH ₄
5A	5	3	NH ₃
6A	6	2	H ₂ O
7A	7	1	HF
8A	8	0	Ne

Electron-Dot Structures of Polyatomic Molecules

Step 3: Assign Electrons to the Terminal Atoms

- Subtract the number of electrons used for bonding in the previous step from the total number determined in step 1.
- Complete each terminal atom's octet (except for hydrogen).

Step 4: Assign Electrons to the Central Atom

- If unassigned electrons remain after step 3, place them on the central atom.

Electron-Dot Structures of Polyatomic Molecules

Step 5: Multiple Bonds

- If no unassigned electrons remain after step 3 but the central atom does not yet have an octet, use one or more lone pairs of electrons from a neighboring atom to form a multiple bond (either a double or a triple).

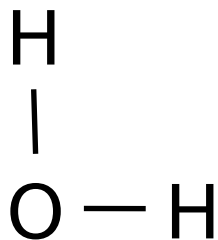
Electron-Dot Structures of Polyatomic Molecules

Draw an electron-dot structure for H_2O .

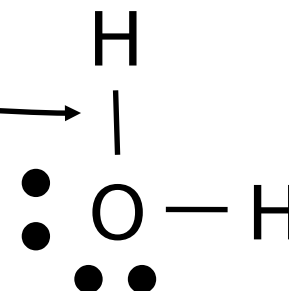
Step 1:

$2 \times (1 \text{ valence } e^- \text{ for each H}) + 1 \times (6 \text{ valence } e^- \text{ for each O})$
 $= 8 \text{ total valence electrons}$

Step 2:



Step 4:



bonding pair of electrons

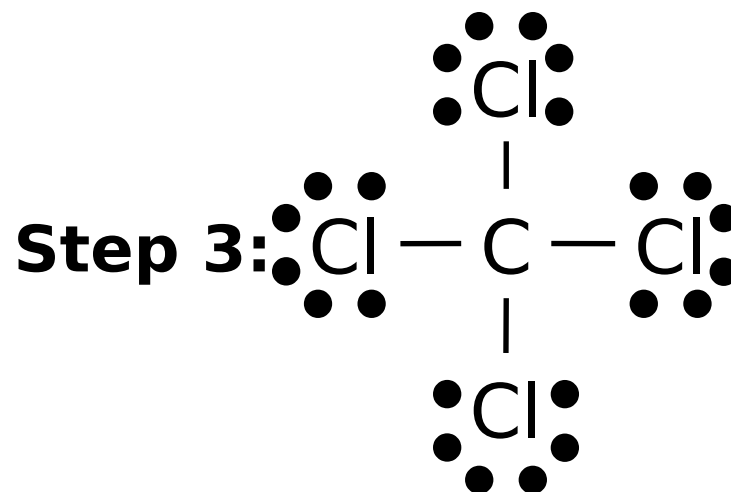
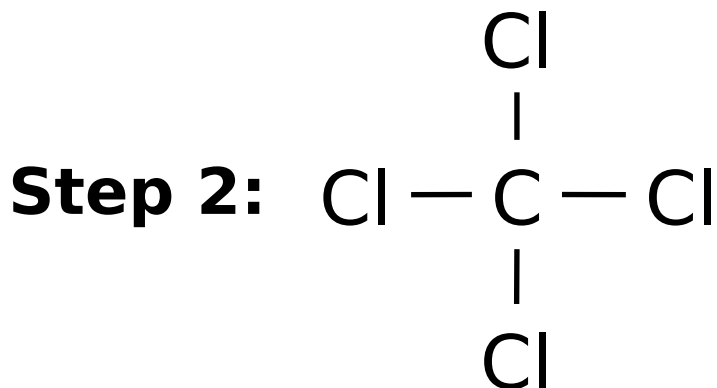
lone pair of electrons

Electron-Dot Structures of Polyatomic Molecules

Draw an electron-dot structure for **CCl₄**.

Step 1:

$1 \times (4 \text{ valence } e^- \text{ for each C}) + 4 \times (7 \text{ valence } e^- \text{ for each Cl})$
 $= 32 \text{ valence electrons}$



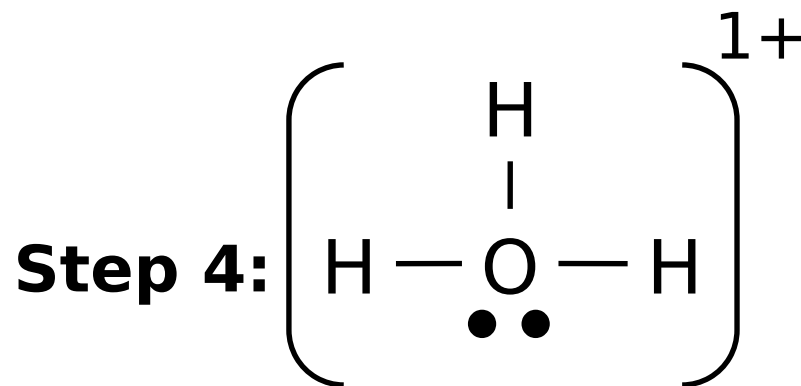
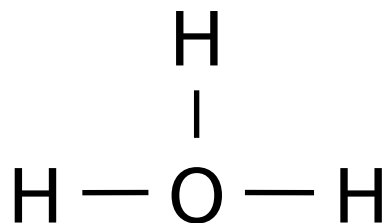
Electron-Dot Structures of Polyatomic Molecules

Draw an electron-dot structure for H_3O^{1+} .

Step 1:

$3 \times (1 \text{ valence } e^- \text{ for each H}) + 1 \times (6 \text{ valence } e^- \text{ for each O})$
 $- 1 \text{ (for the } + \text{ charge on O)} = 8 \text{ total valence electrons}$

Step 2:

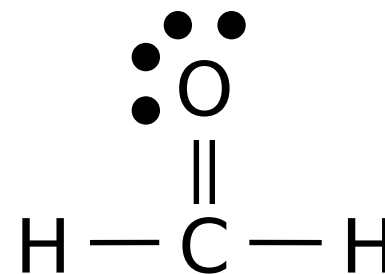
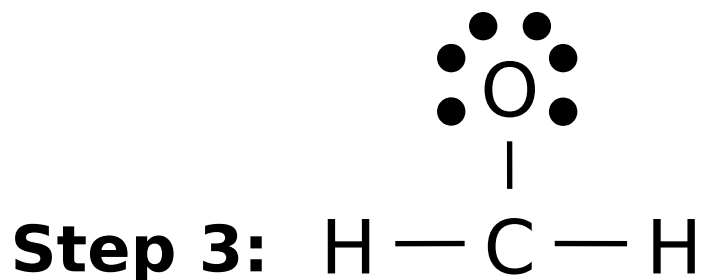
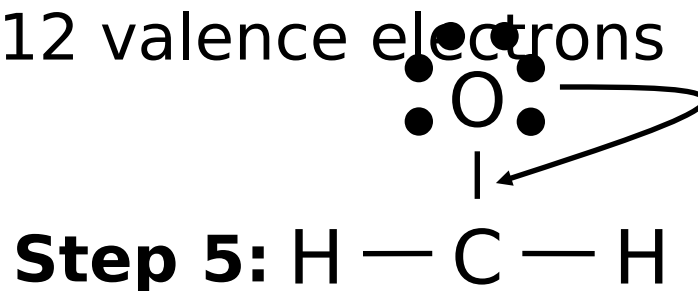
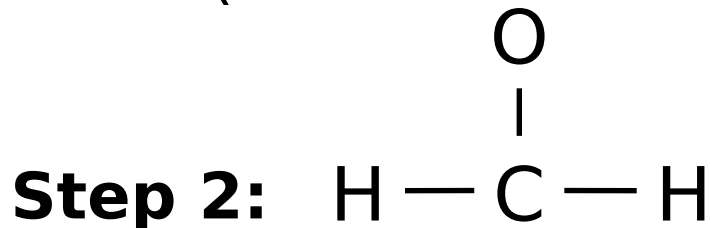


Electron-Dot Structures of Polyatomic Molecules

Draw an electron-dot structure for **CH₂O**.

Step 1:

1x(4 valence e⁻ for each C) + 2x(1 valence e⁻ for each H)
+ 1x(6 valence e⁻ for each O) = 12 valence electrons



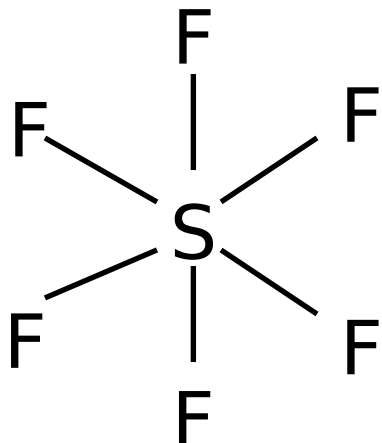
Electron-Dot Structures of Polyatomic Molecules

Draw an electron-dot structure for **SF₆**.

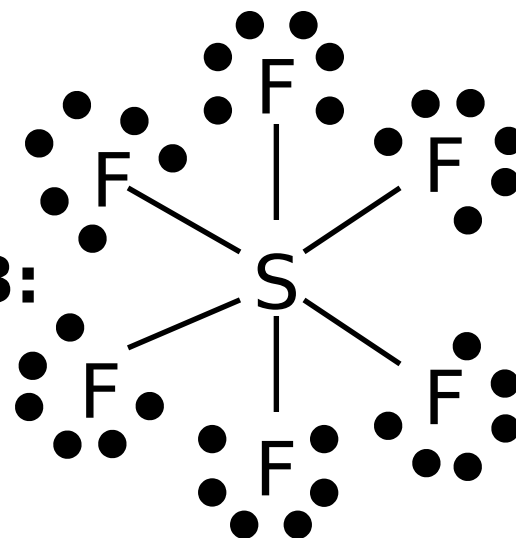
Step 1:

$1 \times (6 \text{ valence } e^- \text{ for each S}) + 6 \times (7 \text{ valence } e^- \text{ for each F})$
 $= 48 \text{ valence electrons}$

Step 2:



Step 3:

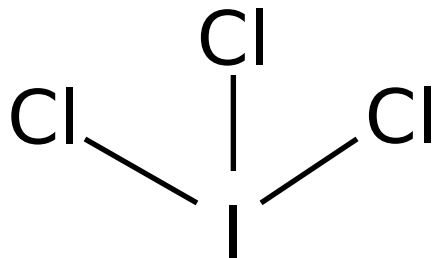


Electron-Dot Structures of Polyatomic Molecules

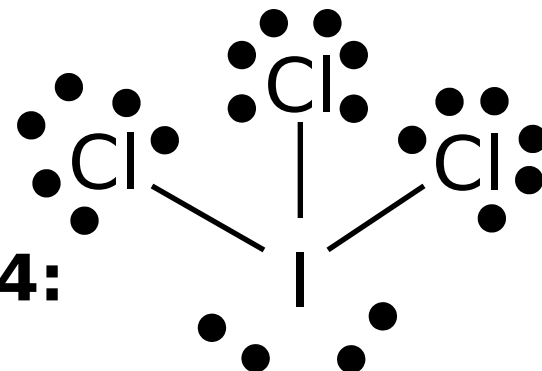
Draw an electron-dot structure for **ICl₃**.

Step 1: $+ 3(7) = 28$ valence electrons

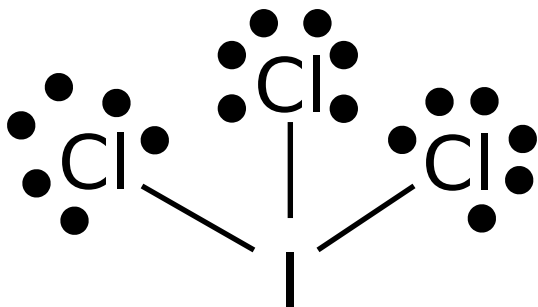
Step 2:



Step 4:



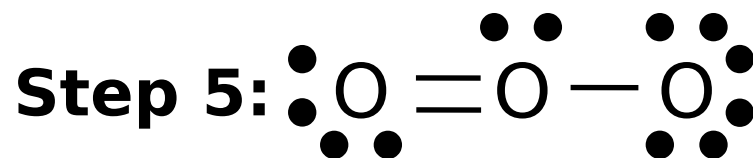
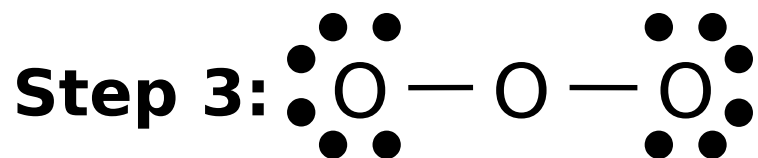
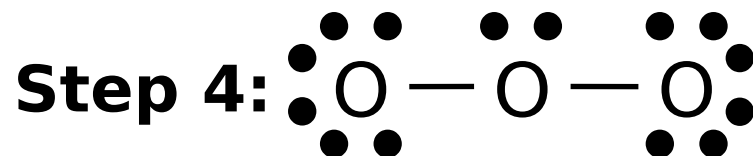
Step 3:



Electron-Dot Structures and Resonance

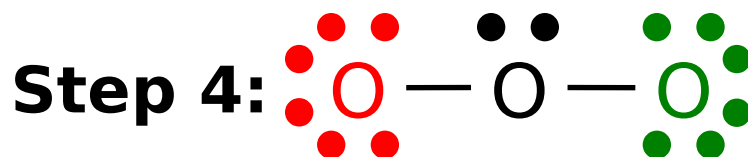
Draw an electron-dot structure for O_3 .

Step 1: $3(6) = 18$ valence electrons

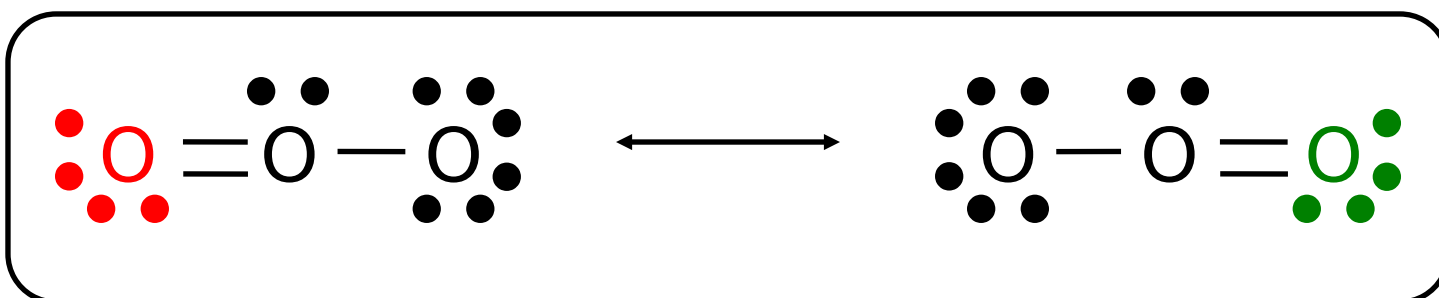


Electron-Dot Structures and Resonance

Move a lone pair from this oxygen?



Or, move a lone pair from this oxygen?

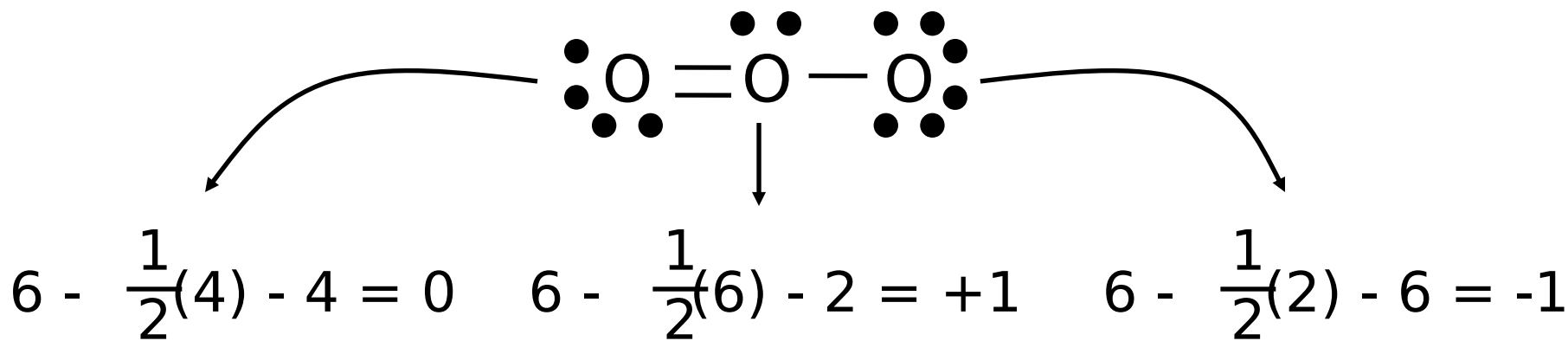


Resonance

Formal Charges

$$\text{Formal Charge} = \left(\begin{array}{c} \# \text{ of} \\ \text{valence } e^- \\ \text{in free atom} \end{array} \right) - \frac{1}{2} \left(\begin{array}{c} \# \text{ of} \\ \text{bonding} \\ e^- \end{array} \right) - \left(\begin{array}{c} \# \text{ of} \\ \text{nonbonding} \\ e^- \end{array} \right)$$

Calculate the formal charge on each atom in O_3 .



Molecular Shapes: The VSEPR Model

VSEPR: Valence-Shell Electron-Pair Repulsion model

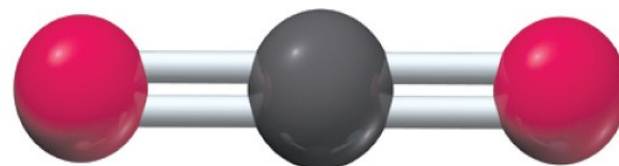
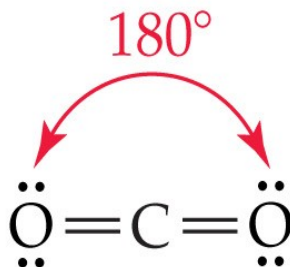
Electrons in bonds and in lone pairs can be thought of as “charge clouds” that repel one another and stay as far apart as possible, this causing molecules to assume specific shapes.

Working from an electron-dot structure, count the number of “charge clouds,” and then determine the molecular shape.

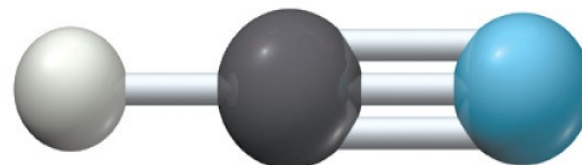
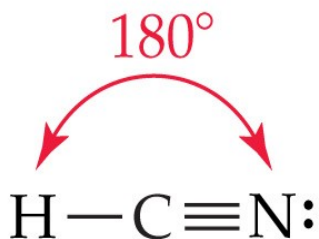
Molecular Shapes: The VSEPR Model

Two Charge Clouds

A CO_2 molecule is linear, with a bond angle of 180° .



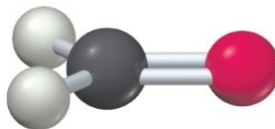
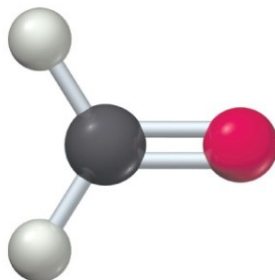
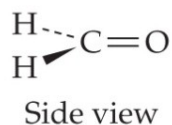
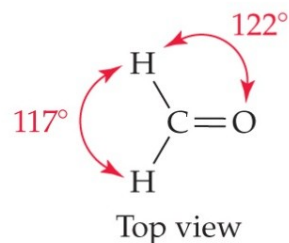
An HCN molecule is linear, with a bond angle of 180° .



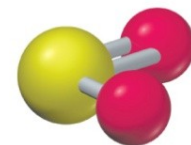
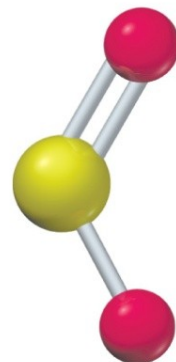
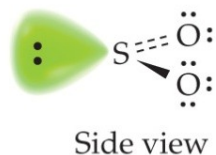
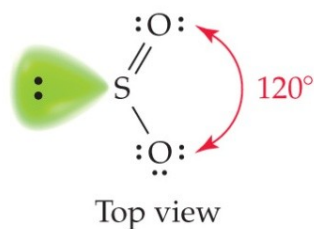
Molecular Shapes: The VSEPR Model

Three Charge Clouds

A formaldehyde molecule is trigonal planar, with bond angles of roughly 120° .

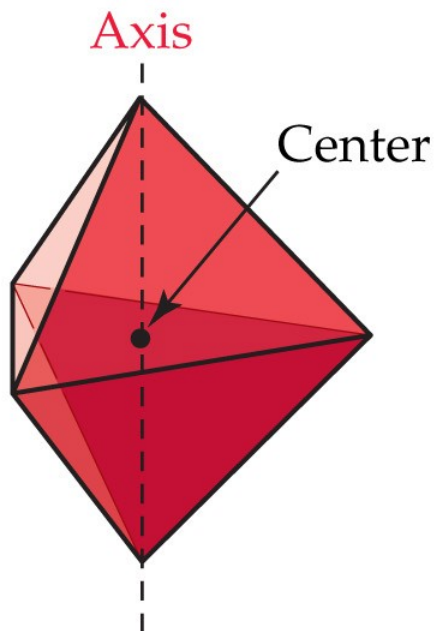


An SO_2 molecule is bent, with a bond angle of approximately 120° .

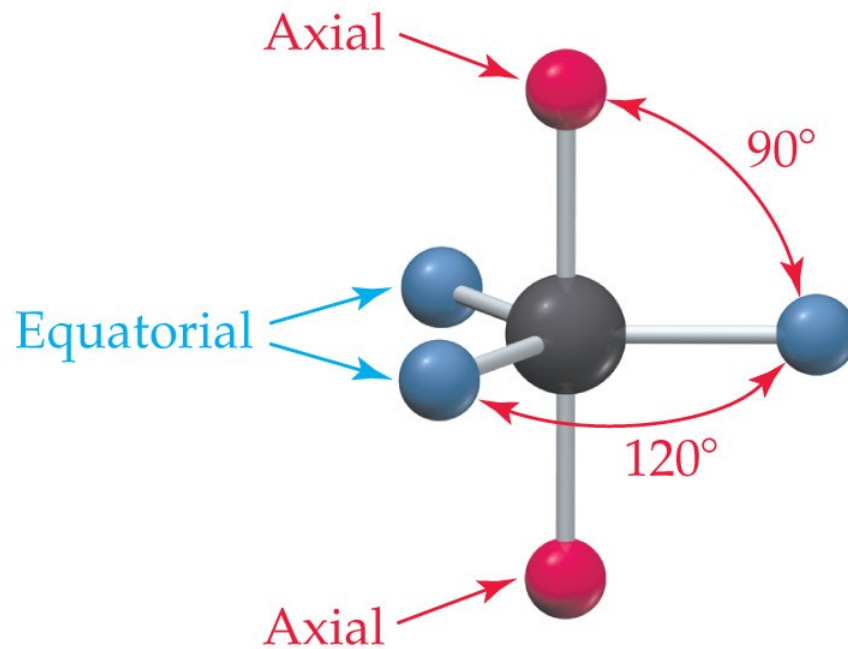


Molecular Shapes: The VSEPR Model

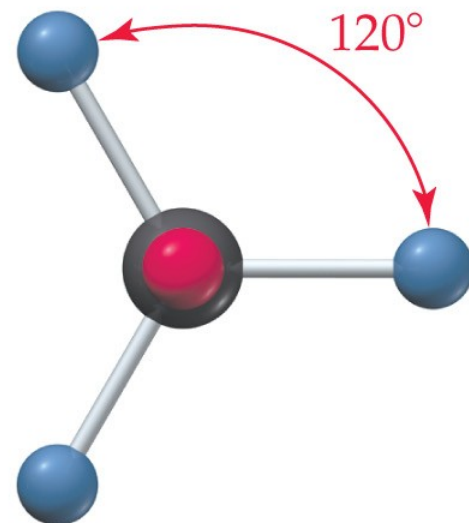
Four Charge Clouds



A trigonal bipyramid



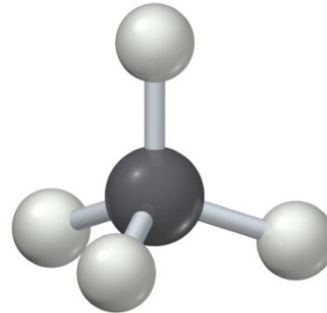
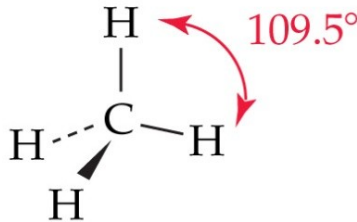
Side view



Top view

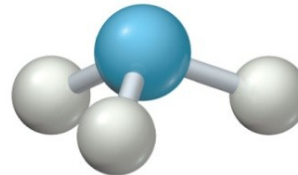
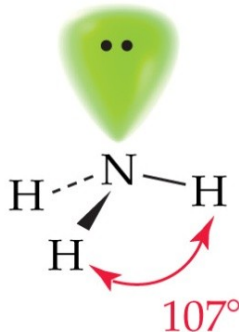
Molecular Shapes: The VSEPR Model

A methane molecule is tetrahedral, with bond angles of 109.5° .

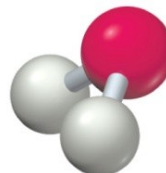
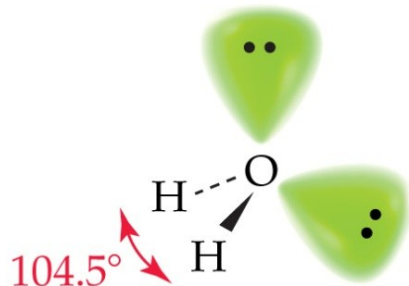


**Four
Charge
Clouds**

An ammonia molecule is trigonal pyramidal, with bond angles of 107° .

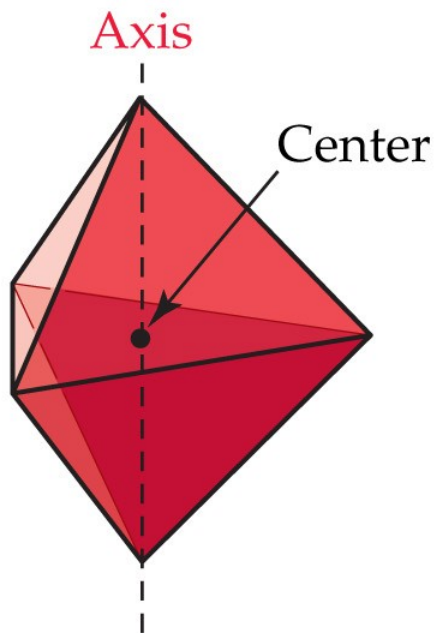


A water molecule is bent, with a bond angle of 104.5° .

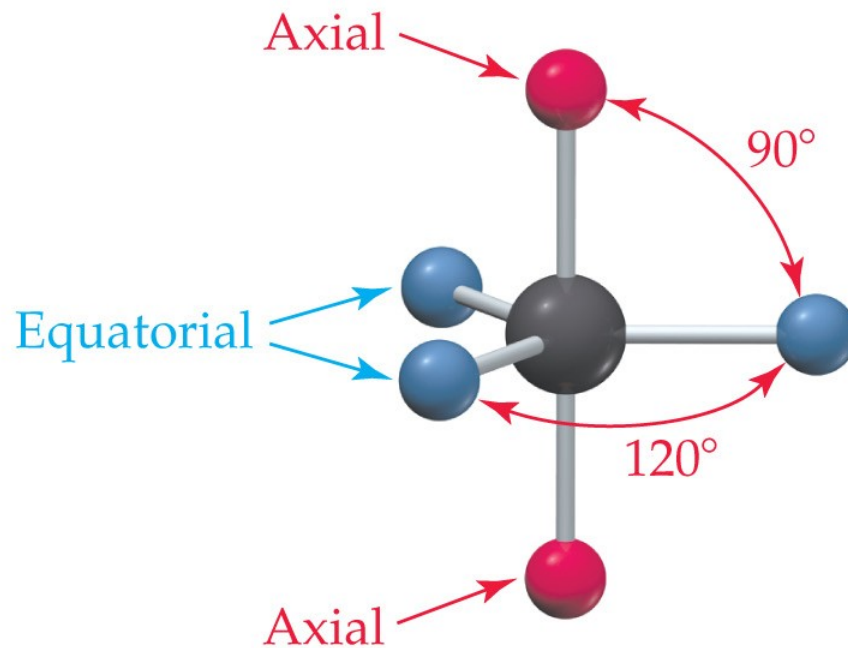


Molecular Shapes: The VSEPR Model

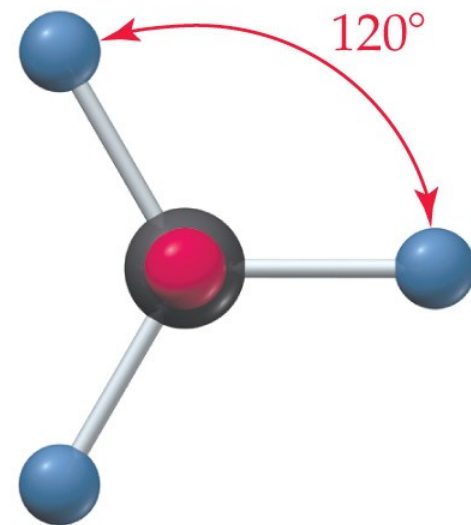
Five Charge Clouds



A trigonal bipyramid



Side view

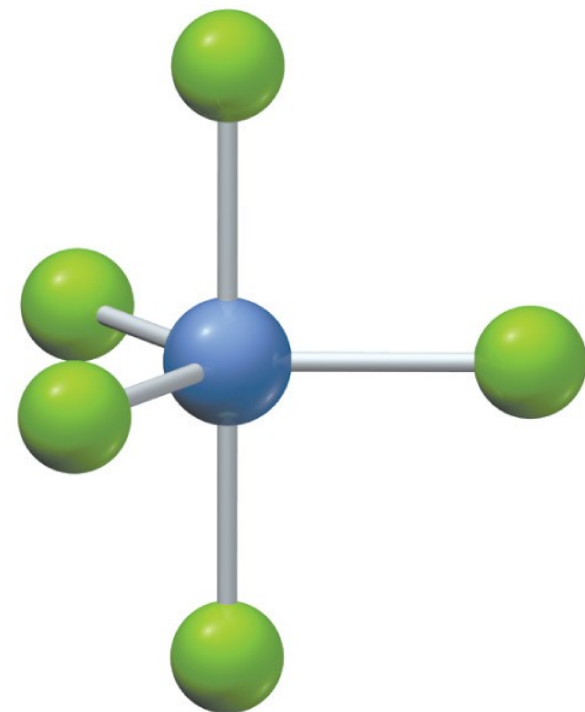
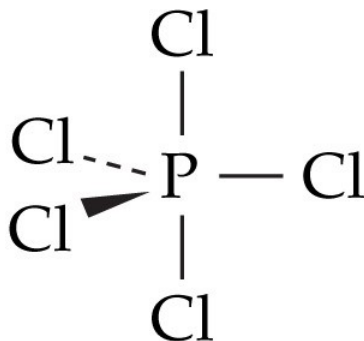


Top view

Molecular Shapes: The VSEPR Model

Five Charge Clouds

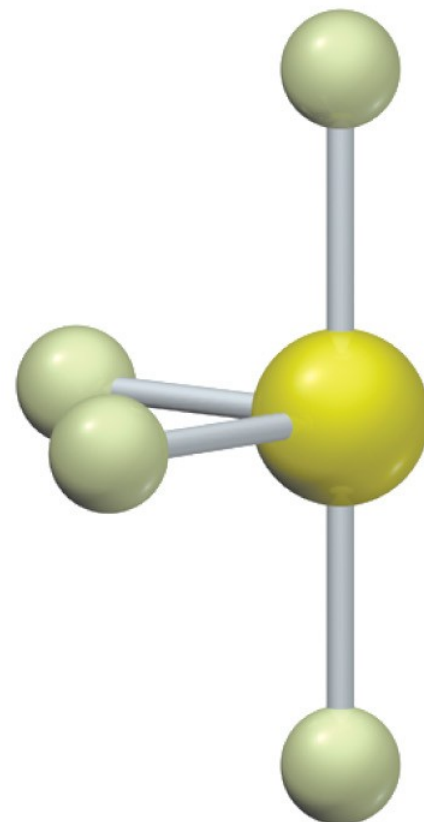
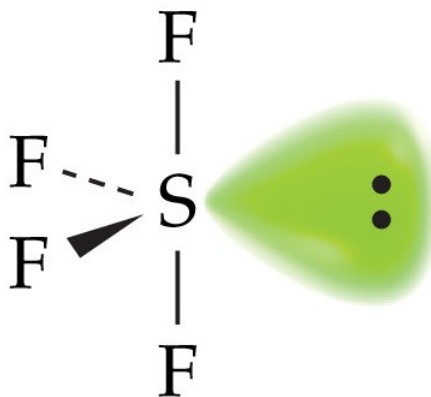
A PCl_5 molecule is trigonal bipyramidal.



Molecular Shapes: The VSEPR Model

Five Charge Clouds

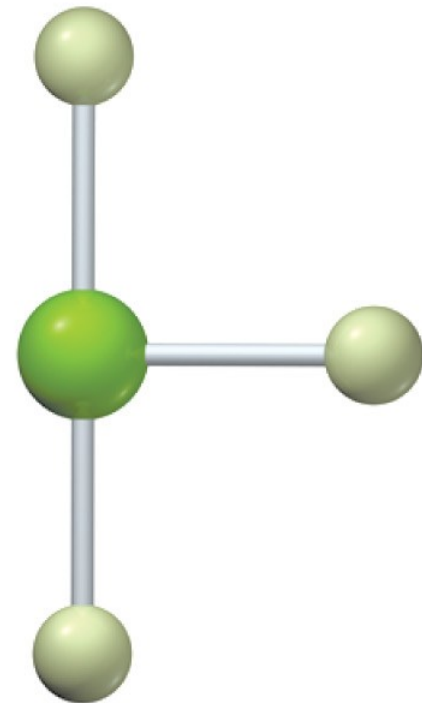
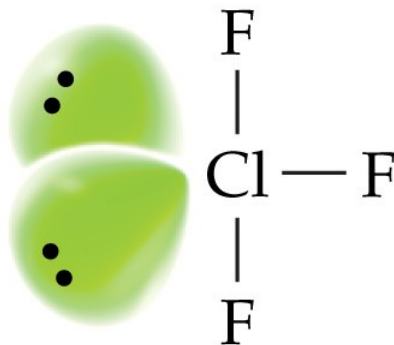
An SF_4 molecule is shaped like a seesaw (turn 90° to see it).



Molecular Shapes: The VSEPR Model

Five Charge Clouds

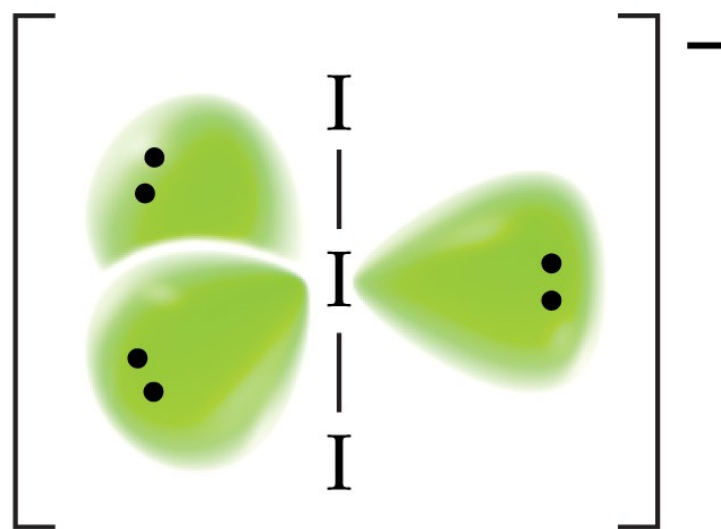
A ClF_3 molecule is T-shaped (turn 90° to see it).



Molecular Shapes: The VSEPR Model

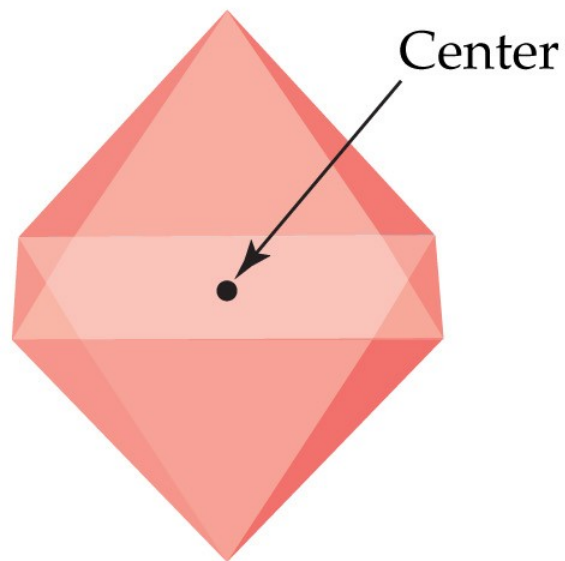
Five Charge Clouds

An I_3^- ion is linear.

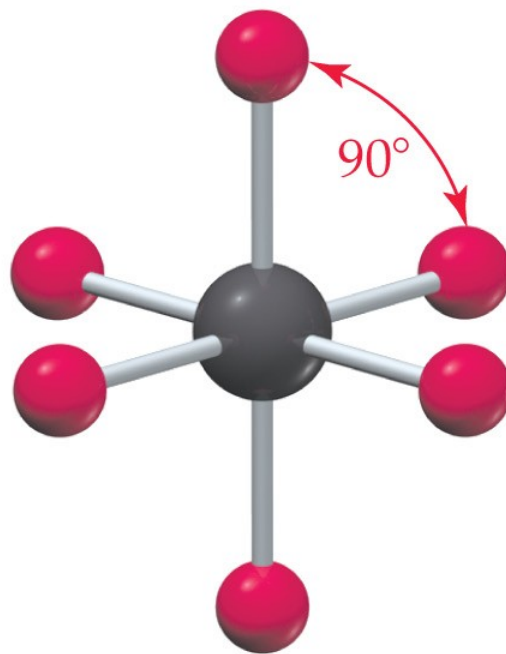


Molecular Shapes: The VSEPR Model

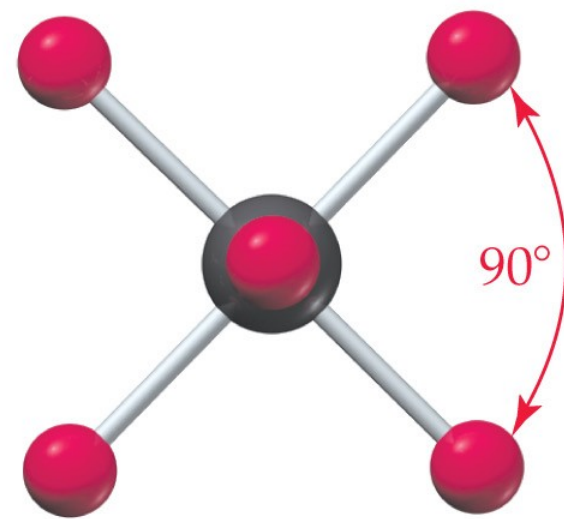
Six Charge Clouds



A regular octahedron



Side view

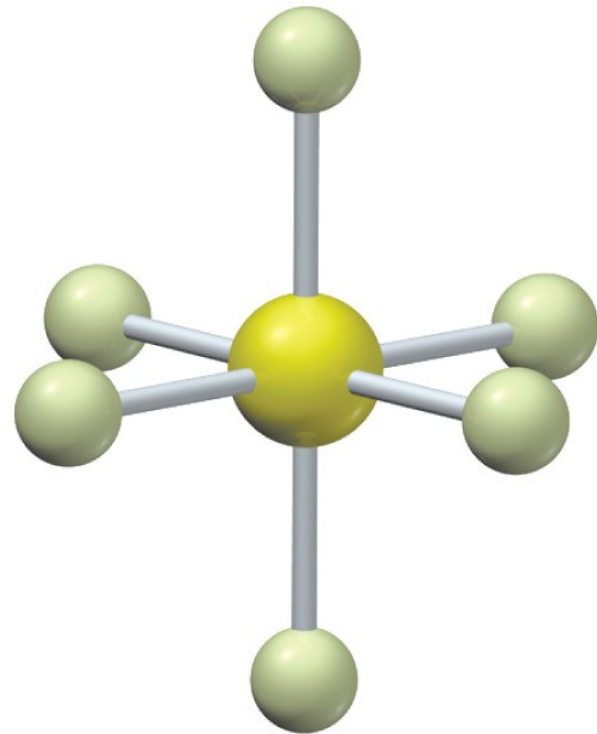
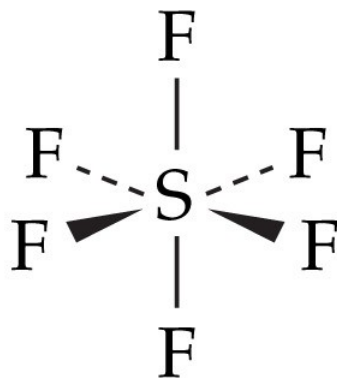


Top view

Molecular Shapes: The VSEPR Model

Six Charge Clouds

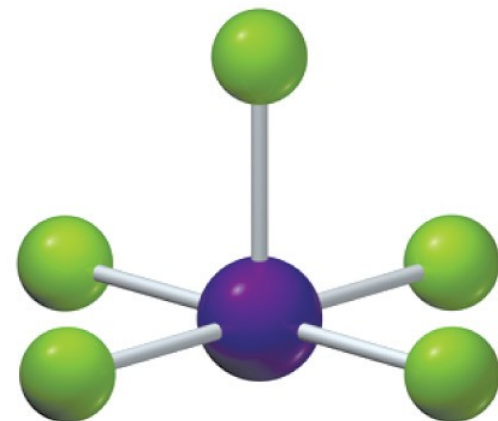
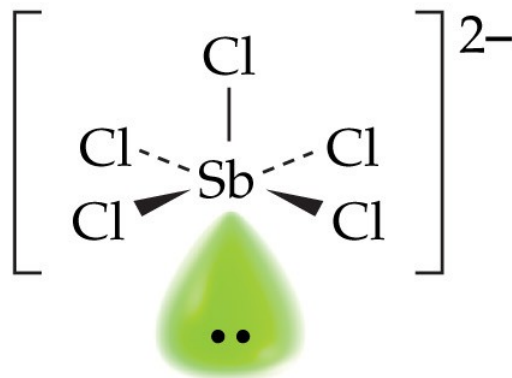
An SF_6 molecule is octahedral.



Molecular Shapes: The VSEPR Model

Six Charge Clouds

An SbCl_5^{2-} ion has a square pyramidal shape.



Molecular Shapes: The VSEPR Model

Six Charge Clouds

An XeF_4 molecule has a square planar shape.

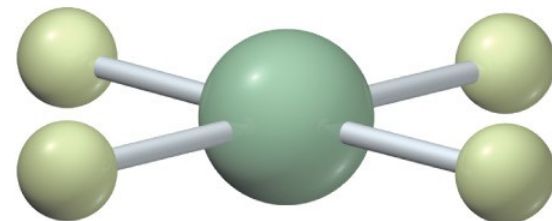
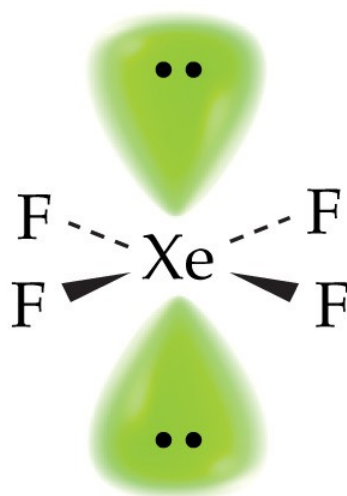


TABLE 5.5 Molecular Geometry Around Atoms with 2, 3, 4, 5, and 6 Charge Clouds

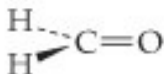
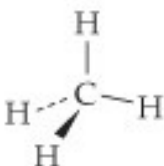
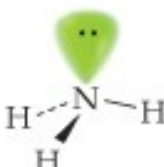
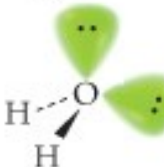
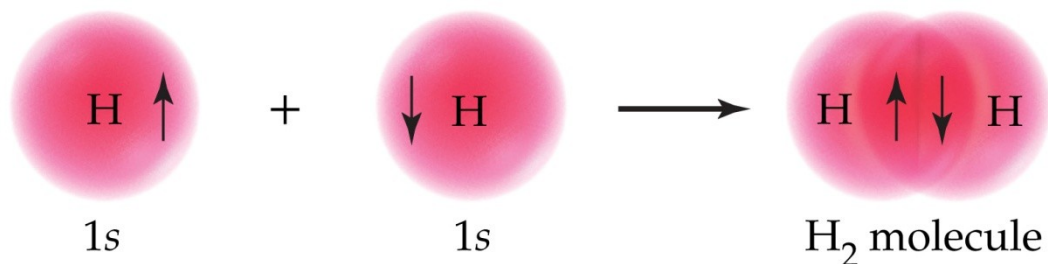
Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
2	0	2	 Linear	$\text{O}=\text{C}=\text{O}$
3 2	0	3	 Trigonal planar	
	1		 Bent	
4 3 2	0	4	 Tetrahedral	
	1		 Trigonal pyramidal	
	2		 Bent	

TABLE 5.5 (Continued)

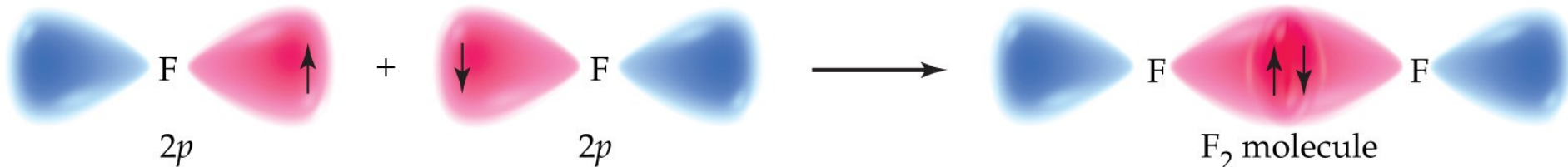
Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
5	0	5	Trigonal bipyramidal	
4	1		Seesaw	
3	2		T-shaped	
2	3		Linear	
6	0	6	Octahedral	
5	1		Square pyramidal	
4	2		Square planar	

Valence Bond Theory

Valence Bond Theory: A quantum mechanical model which shows how electron pairs are shared in a covalent bond.



sigma (σ) bonds



Valence Bond Theory

Valence Bond Theory: A quantum mechanical model which shows how electron pairs are shared in a covalent bond.

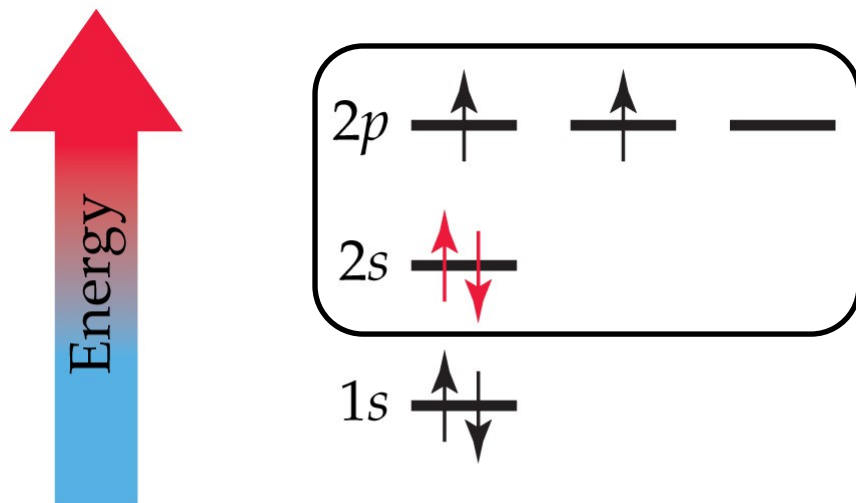
- Covalent bonds are formed by overlap of atomic orbitals, each of which contains one electron of opposite spin.
- Each of the bonded atoms maintains its own atomic orbitals, but the electron pair in the overlapping orbitals is shared by both atoms.
- The greater the amount of overlap, the stronger the bond.

Hybridization and sp^3 Hybrid Orbitals

How can the bonding in CH_4 be explained?

4 valence electrons

2 unpaired electrons

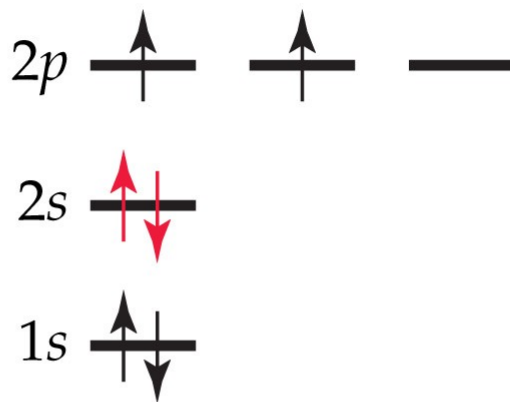


Carbon:
ground-state electron
configuration

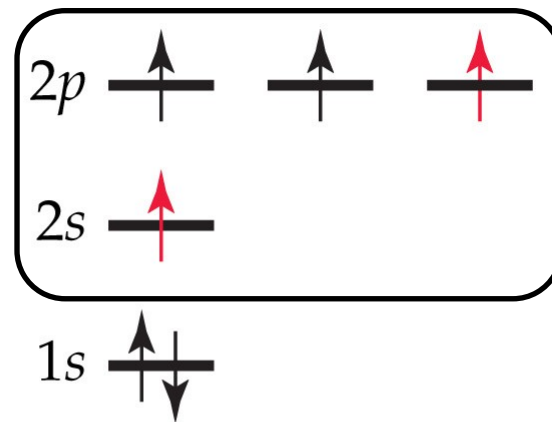
Hybridization and sp^3 Hybrid Orbitals

How can the bonding in CH_4 be explained?

4 valence electrons
4 unpaired electrons



Carbon:
ground-state electron
configuration

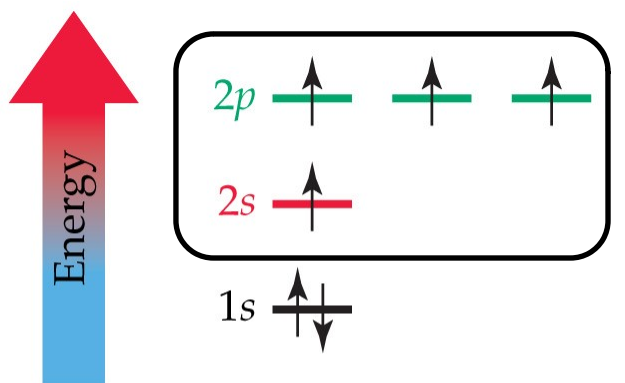


Carbon:
excited-state electron
configuration

Hybridization and sp^3 Hybrid Orbitals

How can the bonding in CH_4 be explained?

4 **nonequivalent** orbitals



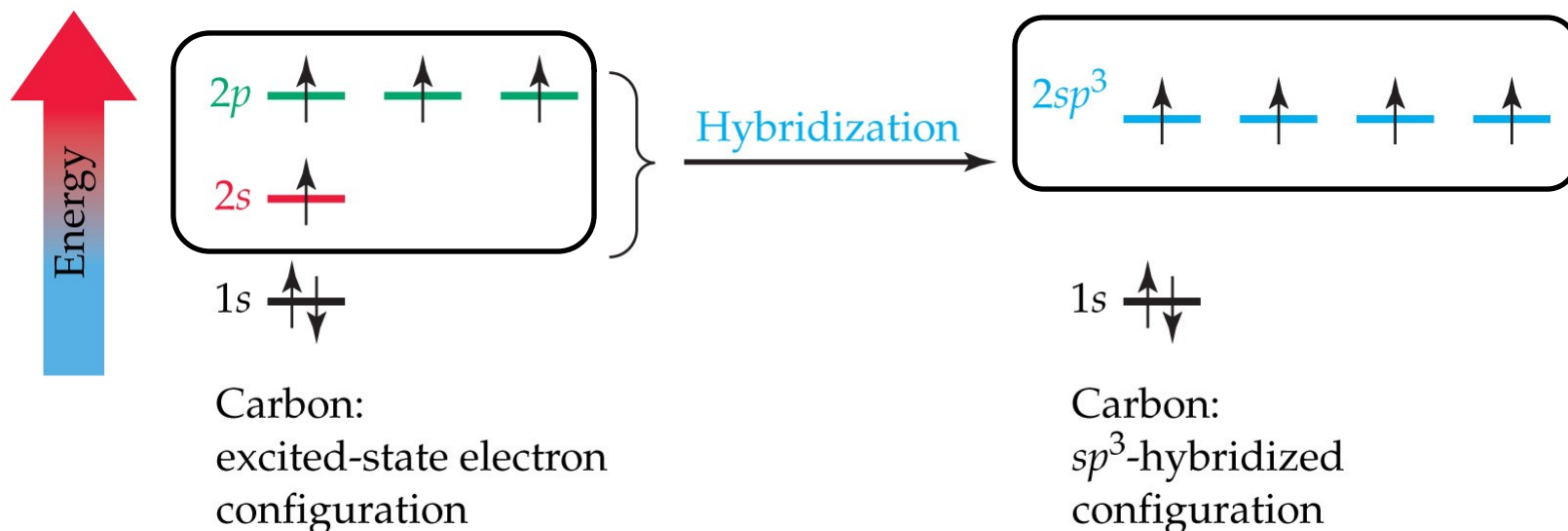
Carbon:
excited-state electron
configuration

Hybridization and sp^3 Hybrid Orbitals

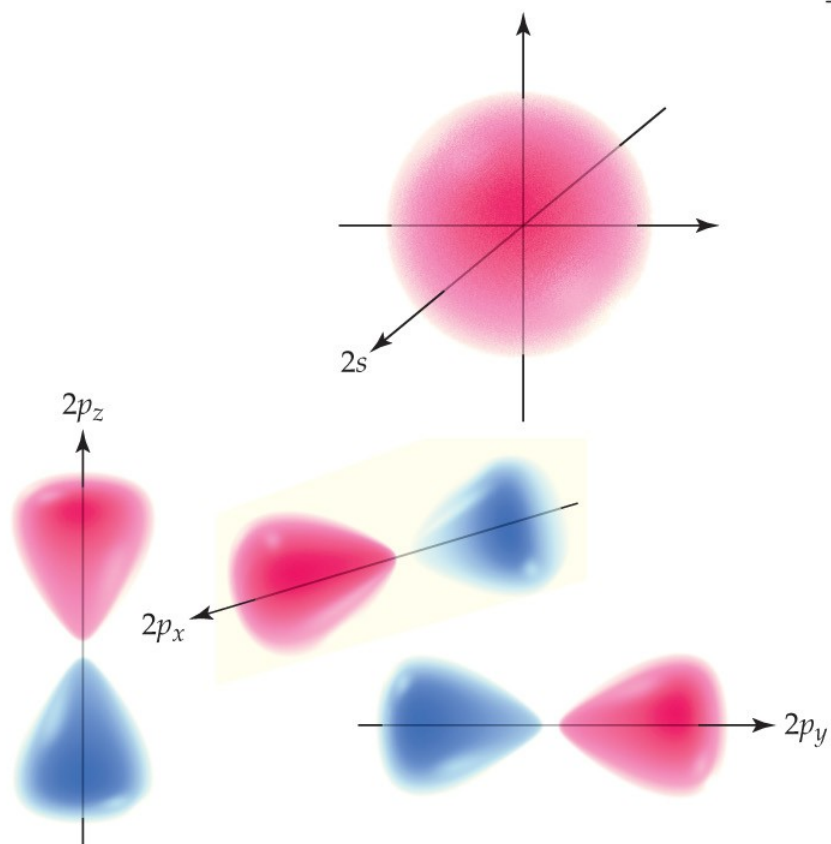
How can the bonding in CH_4 be explained?

4 **nonequivalent** orbitals

4 **equivalent** orbitals



Hybridization and sp^3 Hybrid Orbitals



Each sp^3 hybrid orbital has two lobes, of different phase, one of which is larger than the other



An sp^3 orbital

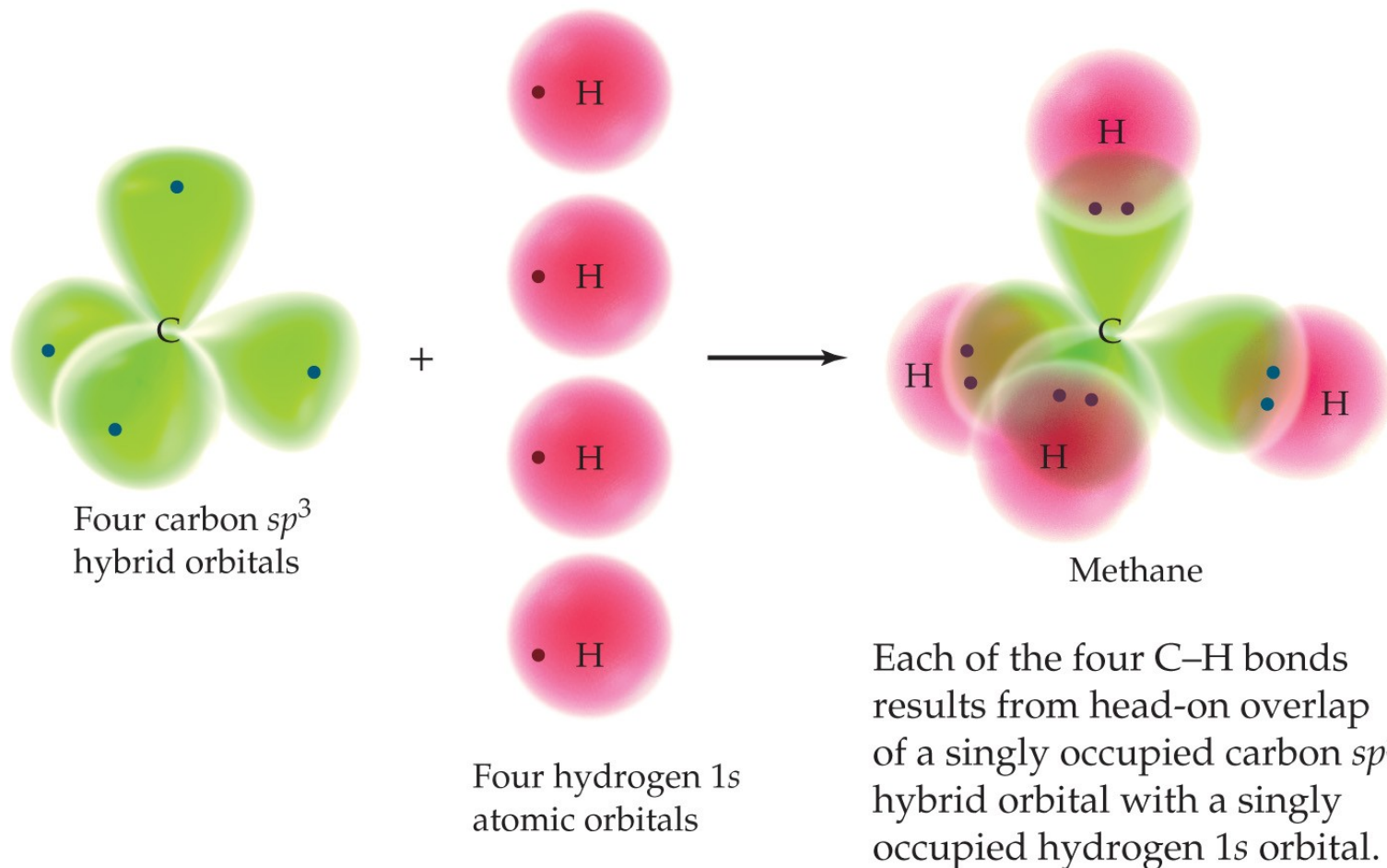
Hybridization



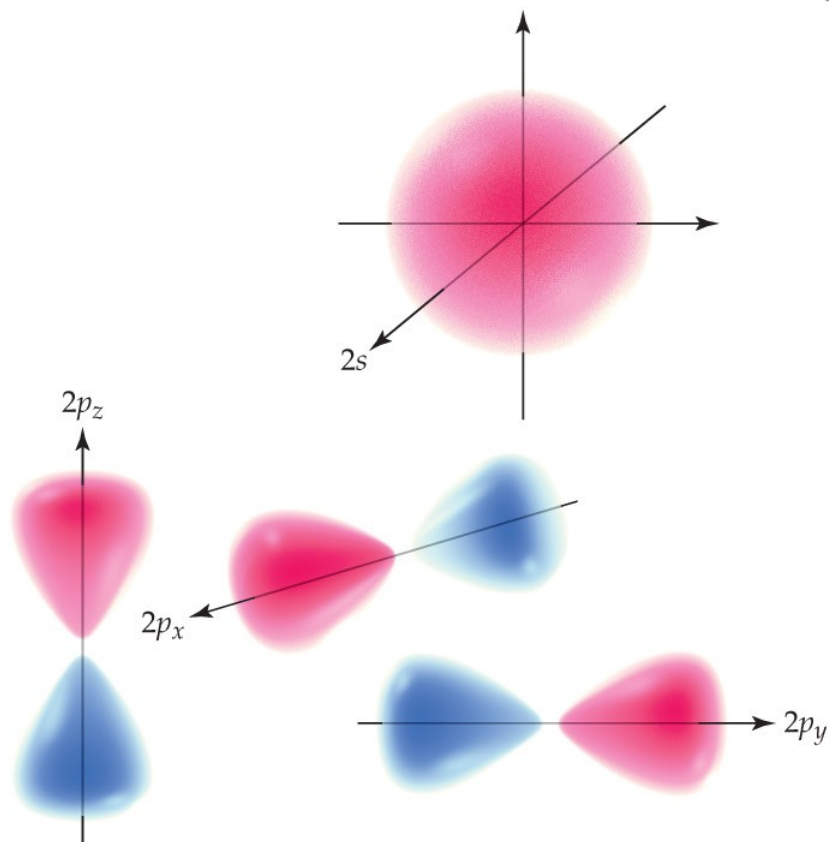
Four tetrahedral sp^3 orbitals

The four large lobes are oriented toward the corners of a tetrahedron at angles of 109.5° . The large lobes of the hybrid orbitals are shown in green, and the small lobes are not shown.

Hybridization and sp^3 Hybrid Orbitals



Other Kinds of Hybrid Orbitals

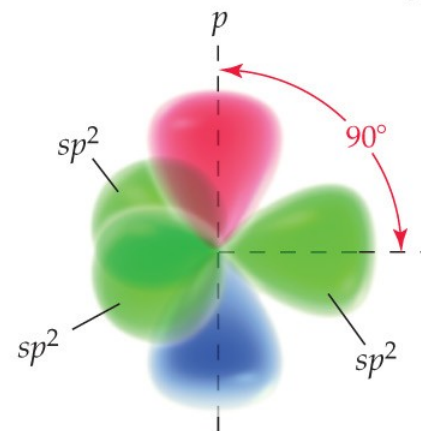


An sp^2 hybrid orbital has two lobes of different phase, one of which is larger than the other.



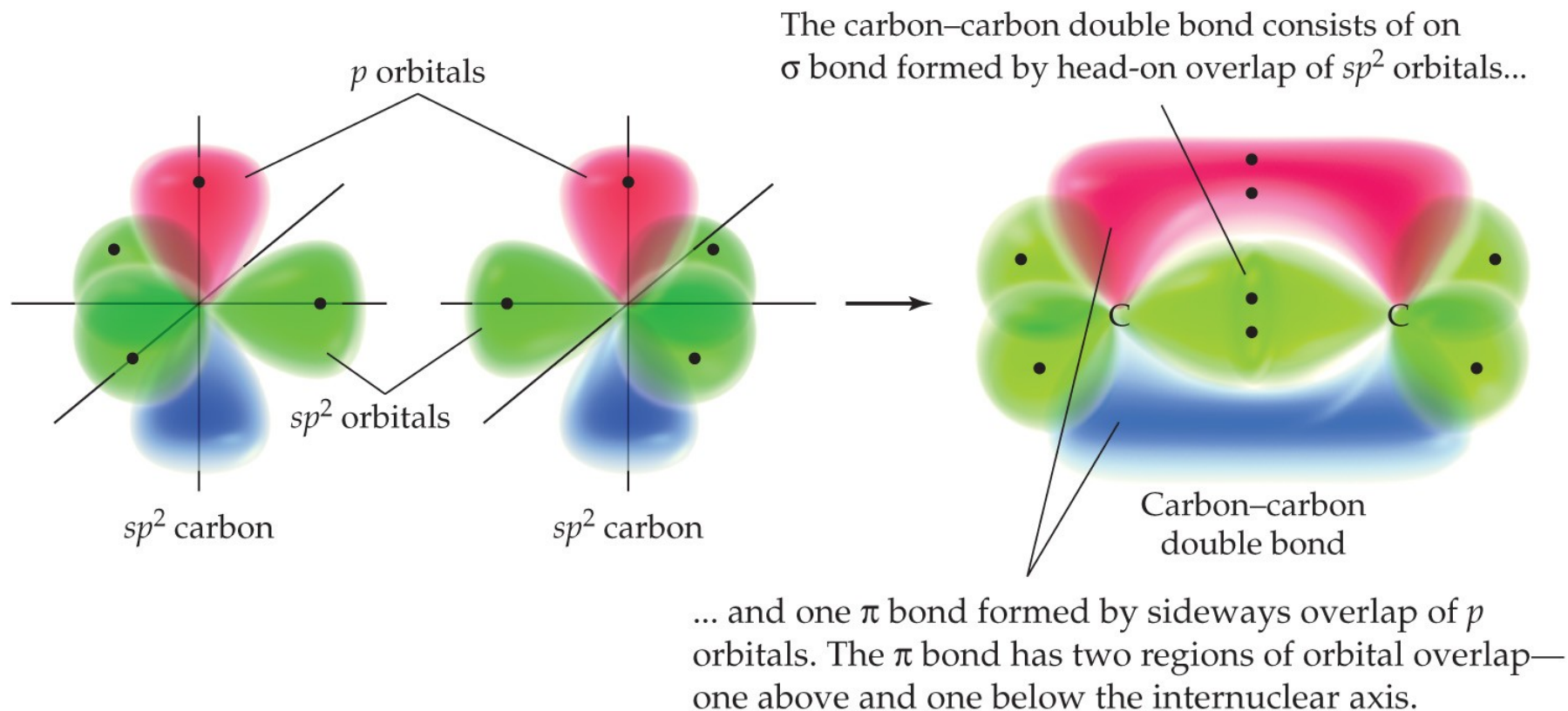
An sp^2 orbital

Hybridization



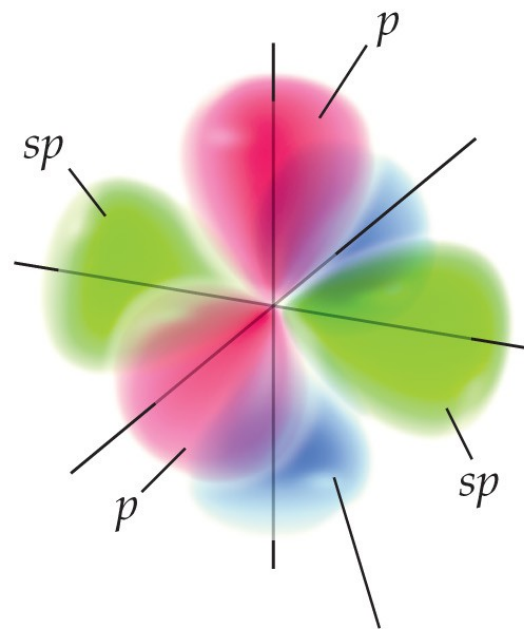
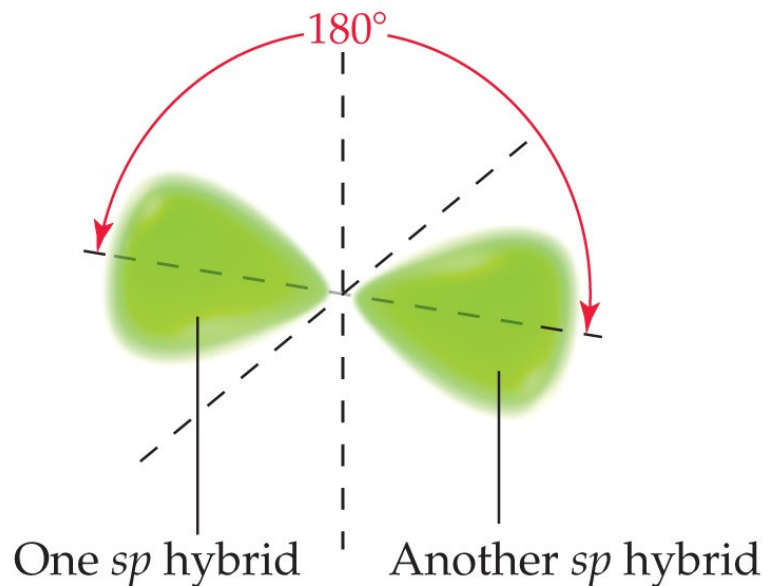
The hybrid orbitals lie in a plane at angles of 120° to one another, and one unhybridized p orbital remains, oriented at a 90° angle to the sp^2 hybrids. The large lobes of the hybrid orbitals are shown in green, and the small lobes are not shown.

Other Kinds of Hybrid Orbitals



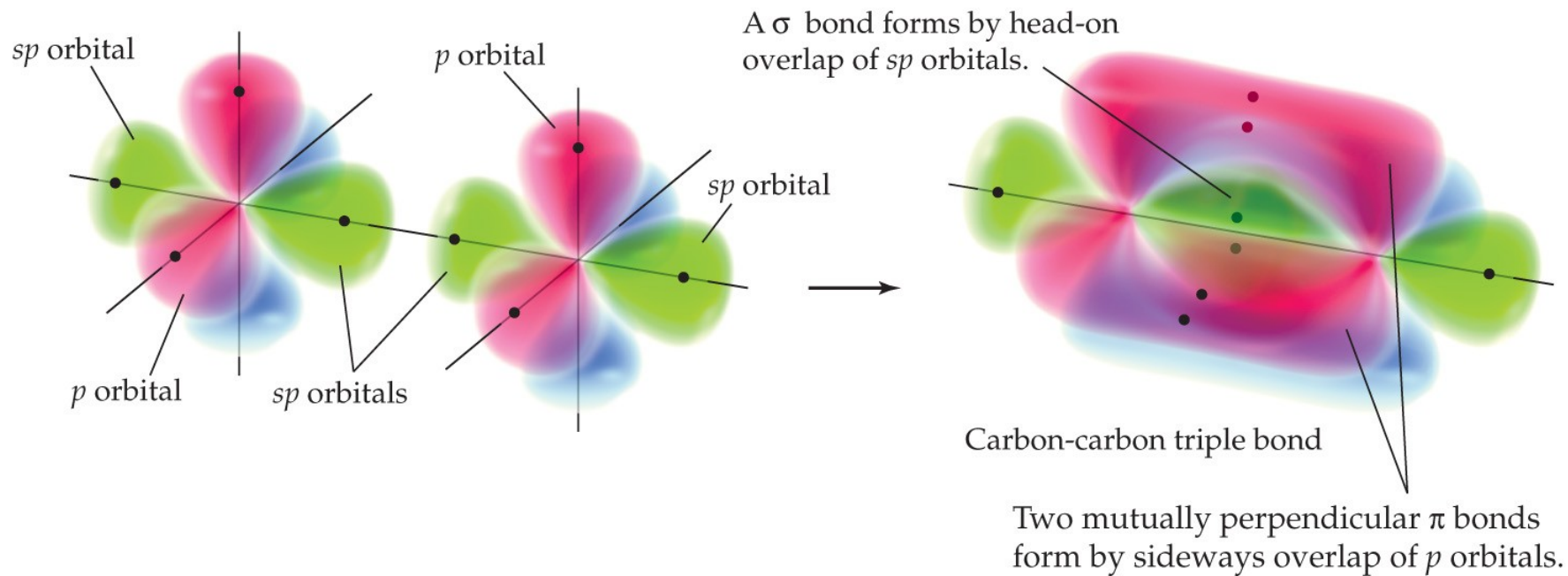
Other Kinds of Hybrid Orbitals

The combination of one s and one p orbital gives two sp hybrid orbitals oriented 180° apart.



In addition, two unhybridized p orbitals remain, oriented at 90° angles to the sp hybrids.

Other Kinds of Hybrid Orbitals



Other Kinds of Hybrid Orbitals

TABLE 5.6 Hybrid Orbitals and Their Geometry

Number of Charge Clouds	Geometry of Charge Clouds	Hybridization
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3

Molecular Orbital Theory: The Hydrogen Molecule

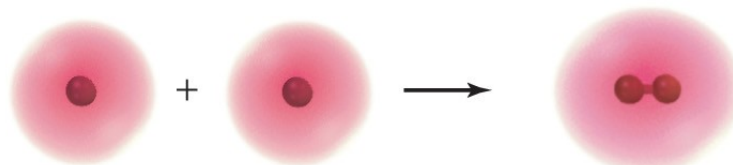
Atomic Orbital: A wave function whose square gives the probability of finding an electron within a given region of space *in an atom*.

Molecular Orbital: A wave function whose square gives the probability of finding an electron within a given region of space *in a molecule*.

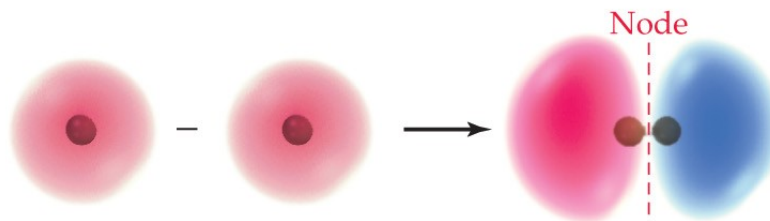
Molecular Orbital Theory: The Hydrogen Molecule

□ bonding orbital
lower in energy

The additive combination of atomic 1s orbitals forms a lower-energy, bonding molecular orbital.



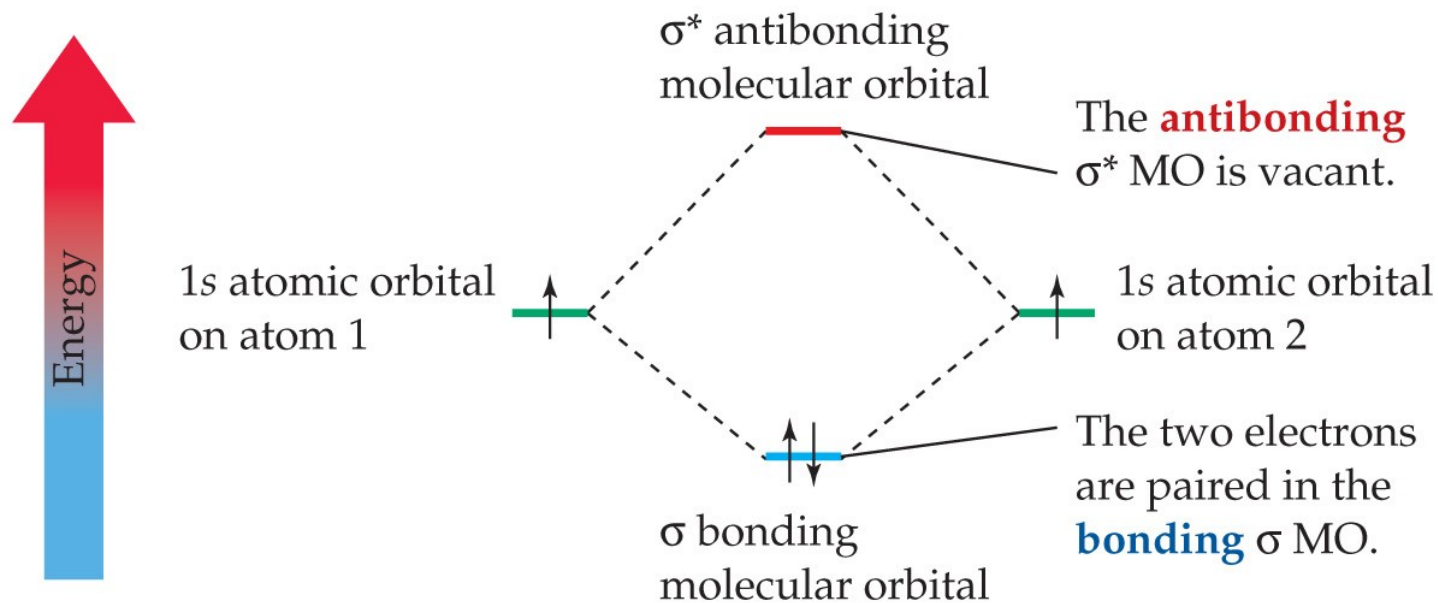
The subtractive combination of atomic 1s orbitals forms a higher-energy, antibonding molecular orbital that has a node between the nuclei.



□* antibonding orbital
higher in energy

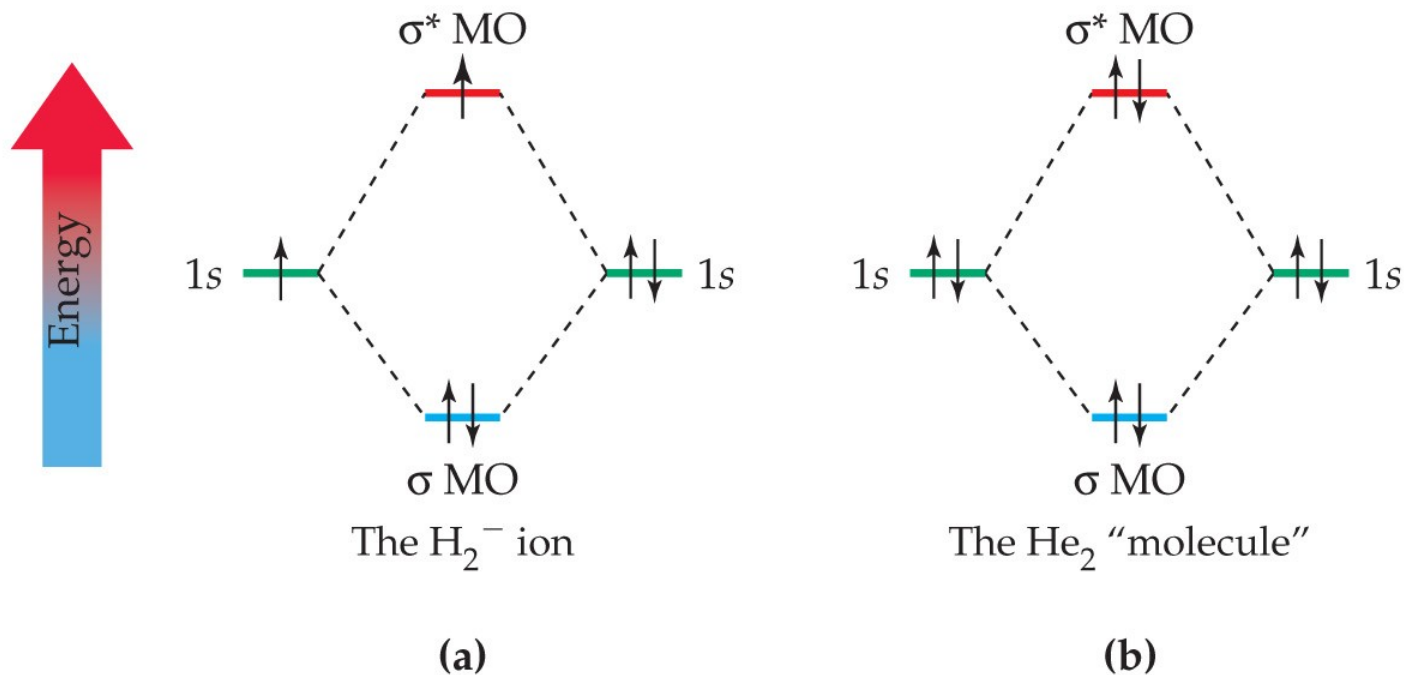
$$\text{Bond Order} = \frac{(\# \text{ Bonding } e^- - \# \text{ Antibonding } e^-)}{2}$$

Molecular Orbital Theory: The Hydrogen Molecule



$$\text{Bond Order} = \frac{2 - 0}{2} = 1$$

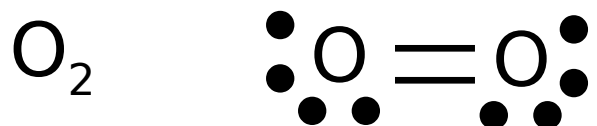
Molecular Orbital Theory: The Hydrogen Molecule



Bond Order: $\frac{2 - 1}{2} = \frac{1}{2}$

$\frac{2 - 2}{2} = 0$

Molecular Orbital Theory: Other Diatomic Molecules

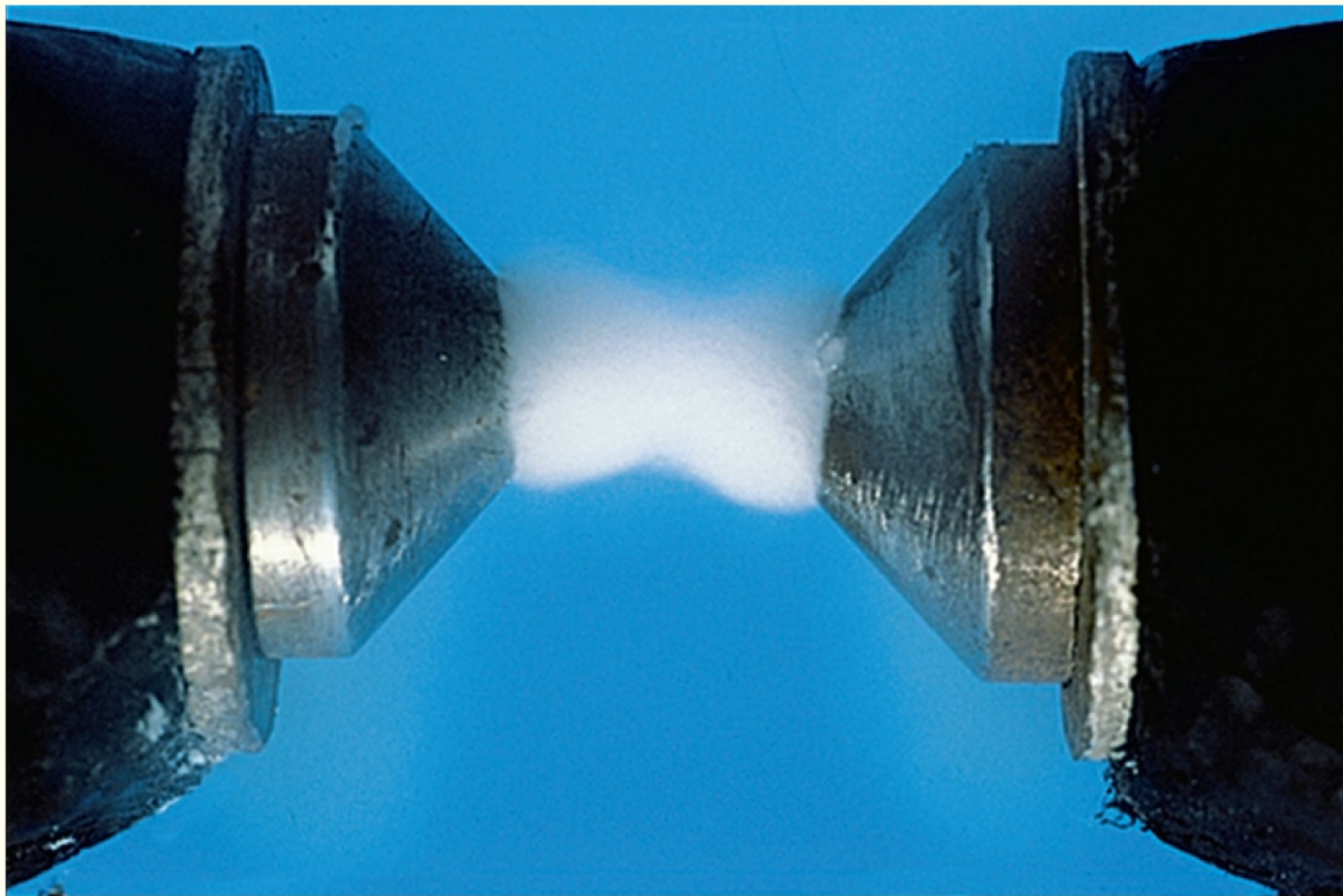


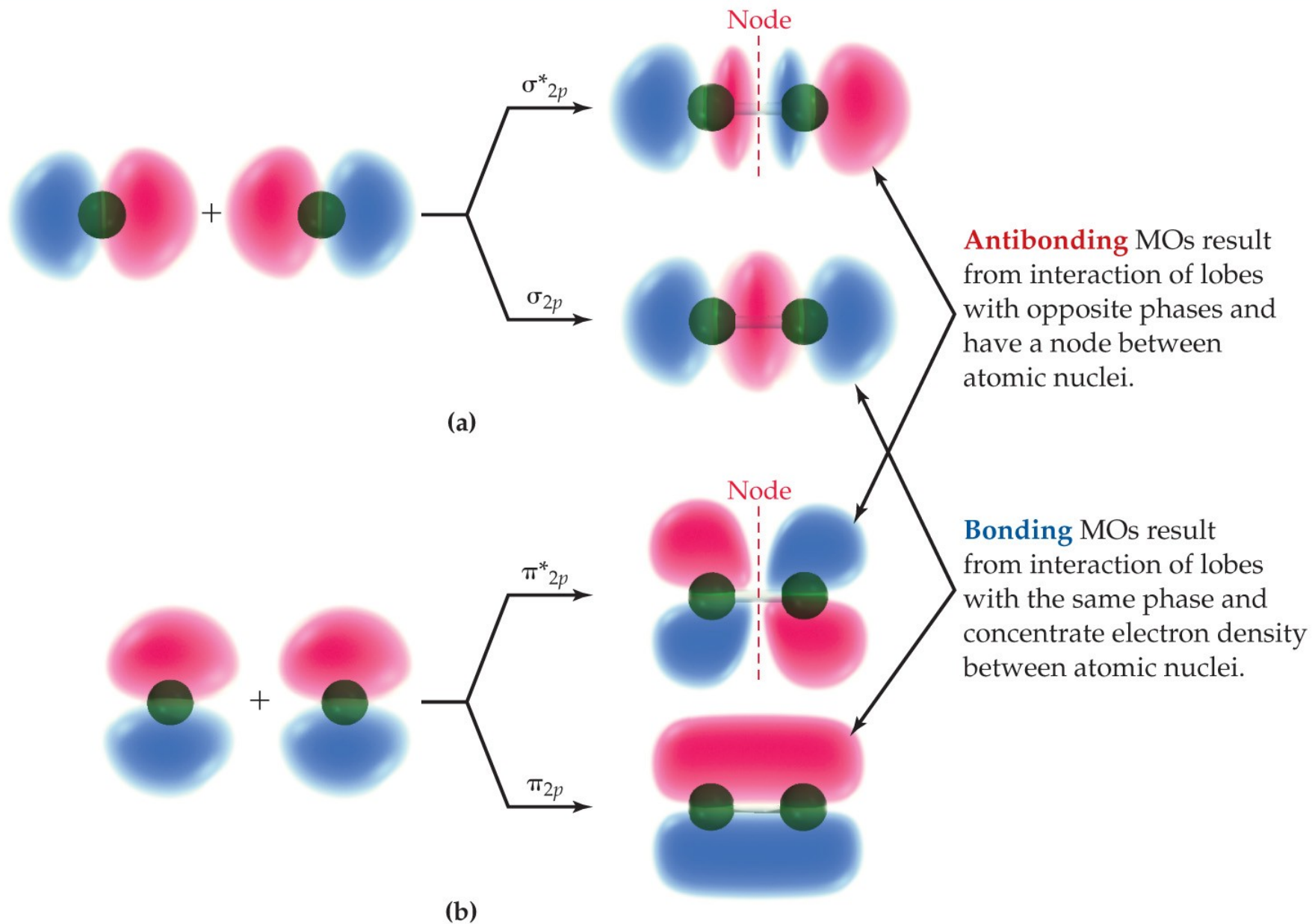
Diamagnetic: All electrons are spin-paired. It is weakly repelled by magnetic fields.

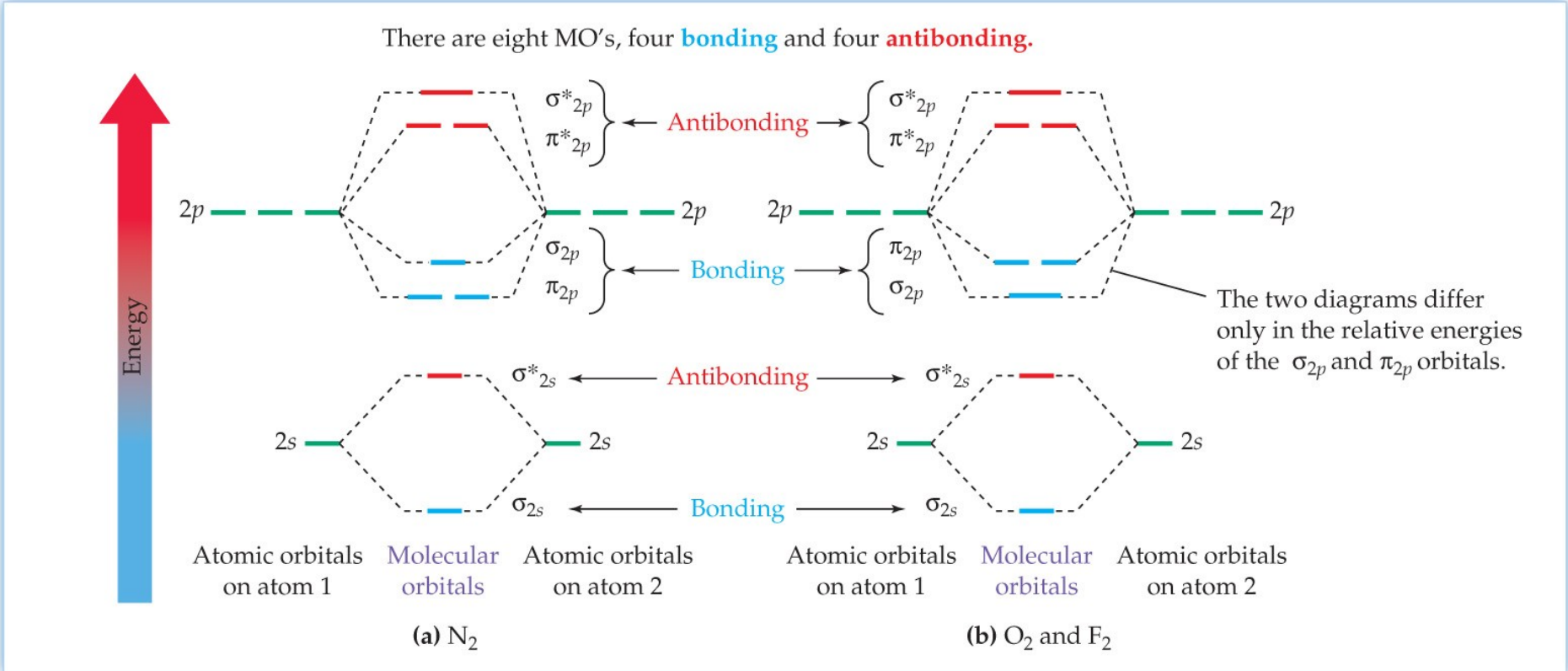
Paramagnetic: There is at least one unpaired electron. It is weakly attracted by magnetic fields.

Oxygen, O_2 , is predicted to be *diamagnetic* by electron-dot structures and valence bond theory.

However, it is known to be *paramagnetic*. Chapter 5/64







Molecular Orbital Theory: Other Diatomic Molecules

